Mathematisches Forschungsinstitut Oberwolfach

Report No. 13/2018

DOI: 10.4171/OWR/2018/13

Mathematical Methods in Quantum Chemistry

Organised by
Eric Cancès, Paris
Gero Friesecke, München
Trygve Ulf Helgaker, Oslo
Lin Lin, Berkeley

18 March – 24 March 2018

Abstract. The field of quantum chemistry is concerned with the modelling and simulation of the behaviour of molecular systems on the basis of the fundamental equations of quantum mechanics. Since these equations exhibit an extreme case of the curse of dimensionality (the Schrödinger equation for N electrons being a partial differential equation on $\mathbb{R}^{3N}$), the quantum-chemical simulation of even moderate-size molecules already requires highly sophisticated model-reduction, approximation, and simulation techniques. The workshop brought together selected quantum chemists and physicists, and the growing community of mathematicians working in the area, to report and discuss recent advances on topics such as coupled-cluster theory, direct approximation schemes in full configuration-interaction (FCI) theory, interacting Green's functions, foundations and computational aspects of density-functional theory (DFT), low-rank tensor methods, quantum chemistry in the presence of a strong magnetic field, and multiscale coupling of quantum simulations.

Mathematics Subject Classification (2010): 81Q05 (81V55, 65Y20).

Introduction by the Organisers

Originally developed for a small number of atoms, quantum-chemical or "ab initio" simulations are nowadays essential tools not just in chemistry but also in materials science, solid-state physics, nanoscience, and molecular biology. A key bottleneck is the computation of the electronic ground or excited states of the system. Since the "exact" electronic Schrödinger equation for a molecule with N electrons is a partial differential equation in $3N$ dimensions, it exhibits an extreme case of the curse of dimensionality: direct simulation on a grid or in standard approximation

subspaces is prohibitive already for a few electrons. Quantum-chemical simulations therefore require highly sophisticated model-reduction, approximation, and simulation techniques. This interdisciplinary workshop brought together quantum chemists, mathematicians, and physicists, focusing on recent conceptual and methodological ideas and (where available) mathematical results.

The contributions by Fabian Faulstich, Heinz-Jürgen Flad, Simen Kvaal, Thomas Bondo Pedersen, and Chao Yang are devoted to the coupled-cluster method, which has been a benchmark method in quantum chemistry for accurate simulation of systems of up to a few dozen electrons for quite some time. Nevertheless, novel understanding – for instance, of its "bi-variational" structure, its singularities at coalescence points, and some subtle numerical challenges – is only now emerging in current research.

The contributions by Jürgen Gauss and Harry Yserentant discuss direct approximability of many-body Schrödinger equation, or FCI wave functions, via, respectively, Gauss–Hermite functions and many-body expansion in the virtual orbital space.

Another, very general and ultimately nonlinear, strategy to capture functions depending on a large number of variables is low-rank tensor approximation. Applications of this strategy – for instance, to the simulation of stationary electronic states and optical spectra – are discussed in the contributions by Venera Khoromskaia and Boris Khoromskij. Christian Lubich summarizes how to carry out robustly dynamical low-rank approximation in the presence of small singular values.

For large systems, the method of choice has for many years been DFT, in which the numerical approximation of the high-dimensional wave function is replaced by a drastic model reduction, focusing on the single-particle density as the key variable. The contributions by Andre Laestadius, Robert van Leeuwen, and Aihui Zhou revisit foundational issues in time-dependent and static DFT. What is rigorously known regarding the existence of the density-to-potential mapping? How can one overcome the lack of functional differentiability of the constrained-search Levy–Lieb functional via functional analytic (Moreau–Yosida) regularization? Computational aspects of DFT – in particular, how to project out an ambient bath and how to compute the exchange–correlation energy efficiently in the random-phase approximation (RPA) – are discussed by Leonardo Zepeda-Núñez and Kyle Thicke, respectively.

Interacting Green's function methods are discussed in the contributions by Michael Lindsey, Lucia Reining, and Reinhold Schneider.

In periodic systems, a highly nontrivial correspondence between the topology and Chern number of the Bloch bundle and the existence of Wannier function is described in the contribution by Gianluca Panati. Antoine Levitt and Anil Damle report on recent advances in the computation of Wannier functions.

Sometimes – for instance in the presence of magnetic fields – it is important to

incorporate effects beyond standard DFT, or even beyond the standard (Born–Oppenheimer–)Schrödinger equation. Andrew Teale discusses recent advances in current-DFT, Erik Tellgren reports on the magnetic Schrödinger–Maxwell model, and Trond Saue discusses the X2C Hamiltonian, which is isospectral to the positive part of the Dirac Hamiltonian despite sacrificing the "small" components of Dirac spinors.

Another important aspect discussed in this report is multiscale coupling of quantum mechanics to molecular mechanics or molecular dynamics. Christoph Ortner discusses electronic relaxation at material defects at the tight-binding level of theory, Benjamin Stamm reports on the effective simulation of solvents, and the contribution by Caroline Lasser is devoted to the emulation of quantum dynamics by stochastic surface hopping.

The richness and diversity of mathematical topics in quantum chemistry presented in this report is rounded off by the contributions by Virginie Ehrlacher, on the inverse problem of designing periodic potentials giving rise to a desired band structure, by Geneviève Dusson, on a-posteriori estimation and post-processing methods for nonlinear eigenvalue problems, by Mathieu Lewin, on the mathematical and physical meaning of critical points of the Hartree–Fock functional, and by Michael Herbst, on a novel basis set for molecular electronic-structure theory, the Coulomb-Sturmians.

Acknowledgement: The MFO and the workshop organizers would like to thank the National Science Foundation for supporting the participation of junior researchers in the workshop by the grant DMS-1641185, "US Junior Oberwolfach Fellows".

Workshop: Mathematical Methods in Quantum Chemistry

Table of Contents

Abstracts

The bivariational principle: status and current developments

Simen Kvaal

In this talk, we review the current status of the analysis of the so-called bivariational principle and bivariational methods for the ground-state energy of a molecular Hamiltonian [1].

The bivariational principle is considered highly unconventional, and was introduced independently by Arponen and Löwdin in the early 1980s [2, 3]. Arponen introduced the principle in the context of coupled-cluster (CC) theory, and his approach demonstrated the possible power of the approach. Yet, the bivariational approach has remained an unconventional view of CC theory, maybe due to the lack of a mathematical foundation.

In quantum mechanics, approximation of eigenvalues of the system Hamiltonian $\hat{H}$ are usually (but not always) approached with the Rayleigh-Ritz variational principle. The Hamiltonian is here assumed to satisfy standard conditions: $\hat{H}$ is below bounded and self-adjoint with domain $D(\hat{H}) \hookrightarrow L^2$. We assume that there exists a ground-state u_0 with eigenvalue E_0. The Rayleigh-Ritz variational principle now states: For any nonzero $u \in D(\hat{H})$, the ground-state eigenvalue satisfies $E_0 \leq \langle u, \hat{H}u\rangle / \langle u, u\rangle$, and equality is obtained precisely when $u = u_0$. Let $H : X \to X'$ be the unique extension of $\hat{H} : D(\hat{H}) \to L^2$ to the form-domain $X \hookrightarrow L^2$, i.e., $H : X \to X'$ is bounded, and for every pair $u, v \in D(\hat{H})$, $\langle u, Hv\rangle = \langle u, \hat{H}v\rangle$.

The Rayleigh quotient is Fréchet smooth on X away from the vanishing denominator, and any eigenpair of $\hat{H}$ is a critical point. Straight-forward differentiation gives the critical point condition

$$\langle v, Hu_*\rangle = E_* \langle v, u_*\rangle , \quad \forall v \in X. \tag{1}$$

Here, $E_* = \langle u_*, Hu_*\rangle / \langle u_*, u_*\rangle$. It is a standard result, that this weak eigenvalue problem is equivalent to the strong eigenvalue problem, i.e., we have that $u_* \in D(\hat{H})$, and thus $\hat{H}u_* = E_*u_*$.

The bivariational principle is a generalization of the Rayleigh-Ritz variational principle that does not assume that $\hat{H}$ is self-adjoint. Consider the bivariate Rayleigh functional

$$\mathcal{E}(u, v) := \frac{\langle u, Hv\rangle}{\langle u, v\rangle}. \tag{2}$$

Then, $\mathcal{E}$ is infinitely Fréchet differentiable at all points $(u, v) \in X \times X$ for which $\langle u, v\rangle \neq 0$. The bivariational principle is as follows: A point (u_*, v_*) is a critical point of $\mathcal{E}$ with critical value $E_* = \mathcal{E}(u_*, v_*)$ if and only if

$$\hat{H}v_* = E_*v_*, \quad \hat{H}^\dagger u_* = \overline{E_*}u_*, \quad \langle u_*, v_*\rangle \neq 0. \tag{3}$$

Under the additional knowledge that $\hat{H}$ is self-adjoint, and assuming a simple eigenvalue for simplicity, we know that $u_* = \alpha v_*$ for some $\alpha \neq 0$. We have here assumed that the weak eigenvalue problem is equivalent to the strong eigenvalue problem for $\hat{H}$ and $\hat{H}^\dagger$, a property which can be verified for operators that are more general than self-adjoint operators [4]. In this talk, we will however assume that $\hat{H}^\dagger = \hat{H}$.

For traditional variational approximations, like Hartree-Fock or configuration-interaction, one minimizes the Rayleigh quotient over some submanifold $\mathcal{M} \subset X$. The below boundedness of the Rayleigh quotient now guarantees that this approximation to the ground-state eigenvalue E_0 will have a quadratic error, which will improve as $\mathcal{M}$ grows.

The idea behind the bivariational principle is to introduce approximate schemes where *different* approximations are being used for u_0 and v_0. This allows greater flexibility at the cost of doubling the number of discrete degrees of freedom. For the bivariational principle, we note that $\mathcal{E}$ is not below bounded, so we cannot in general use arbitrary submanifolds $\mathcal{M} \subset X \times X$, in contrast to the Rayleigh-Ritz approach. Instead, we appeal to nonlinear functional analysis and monotonicity results in the vein of Zarantanello's Theorem [5].

Lacking a sure-fire way of introducing arbitrary manifolds $\mathcal{M}$, we instead approach the problem by introducing a reparametrization map $\Phi : Y \times Y \to X \times X$, where Y is some Hilbert space. The map Φ is assumed to be (locally) one-to-one and onto, and also smooth with a smooth inverse for simplicity. This induces a new functional $\tilde{\mathcal{E}} = \mathcal{E} \circ \Phi$, and we obtain that the original eigenvalue problem is equivalent to finding $y_* \in Y \times Y$ such that $\partial \tilde{E}(y_*) = 0$. We then seek properties of the map Φ such that some sort of local strong monotonicity holds near y_*. Zarantonello's Theorem on local form then implies that taking a sequence of Galerkin spaces $Y_h \subset Y$ will lead to a convergent sequence of critical points and values $y_{*,h}$ and $E_{*,h}$, respectively. Such an approach was recently taken to study the particular case of Arponen's extended CC method [6].

In this talk, we outline how sufficient conditions on Φ can be found, such that the local strong monotonicity holds. The set of sufficient conditions allow error estimates for several methods from quantum chemistry, including the coupled cluster (CC) method in its standard formulation (i.e., the CC with singles-and-doubles, CCSD, with triples, CCSDT, etc, hierarchy). These conditions cover what is known as single-reference methods, and are applicable when the ground state u_0 has single-reference nature.

For Hamiltonians with multi-reference ground states, we need more general conditions, and we outline these as well. We also outline how we can devise novel multi-reference CC-like methods using the bivariational principle.

This work has received funding from the ERC-STG-2014 under grant agreement No 639508.

References

[1] S. Kvaal, Manuscript in preparation (2018).
[2] J.S. Arponen, *Variational Principles and Linked-Cluster* exp *S Expansions for Static and Dynamic Many-Body Problems*, Ann. Phys., **151**, pp. 311–382, (1983).
[3] P.-O. Löwdin, *On the stability problem of a pair of adjoint operators*, J. Math. Phys., **24**, pp. 70–87, (1982).
[4] K. Schmüdgen, *Unbounded Self-adjoint Operators on Hilbert Space*, Graduate Texts in Mathematics 265, Springer, (2012).
[5] E. Zeidler, *Nonlinear Functional Analysis and its Application II/B*, Springer, (1990).
[6] A. Laestadius and S. Kvaal, *Analysis of the extended coupled-cluster method in quantum chemistry*, SIAM J. Numer. Anal., **56**, pp. 660–683, (2018).

Numerical Methods for Solving Coupled Cluster Equations

Chao Yang

(joint work with Jiri Brabec, Jinmei Zhang, Karol Kowalski and Edward Valeev)

We examine two different approaches for accelerating numerical solutions of the couple cluster equations which are known to be nonlinear and highly complex. The first approach is based on the Jacobian-free Newton-Krylov method. We show that method tends to be more stable than the widely used DIIS method when the Jacobian of the coupled clustered equation is not dominated by a diagonal matrix consisting of the differences between the Hartree-Fock occupied and virtual orbital energies. We discuss the possibility of combining the Newton-Krylov method with DIIS method, although this combination does not seems to lead to a significant improvement in convergence rate, at least not for problems that are well behaved. We point out the importance of using level-shifting to regularize diagonal preconditioner consisting of HF orbital energy differences and stabilize the convergence of the Newton-Krylov method for problems that have nearly degenerate orbital energies. We also discuss the possibility of using alternative preconditioners that are based on the construction of a small active space approximation to the coupled cluster equation-of-motion Hamiltonian.

In the second approach, we discuss methods that try to exploit sparsity and low rank structures of the coupled cluster amplitude. In our earlier work [1], we developed a practical numerical scheme to sparsify the correction to coupled cluster amplitudes in an inexact Newton iteration. We showed that 90% of the correction amplitude can be discarded without affecting the convergence of the inexact Newton method. When combined with a tensor contraction scheme that keeps a few additional intermediate tensors and an efficient block sparse contraction procedure, we can improve the overall performance of the inexact Newton solver by a factor of 2 to 3.

Recently, we explored the possibility of using iterative pair natural orbital (PNO) method to reduce the complexity of the coupled cluster equation solver. The PNO's, which was developed many years ago in the work of [3, 4], and regained interest in the recent work of [5], yields a compact representation of the coupled cluster amplitudes. By projecting the coupled cluster equations into the

subspace spanned by PNO's, we can reduce the cost of solving the nonlinear equation significantly. The previous use of PNO's [5] performs a one-shot calculation that uses PNO's constructed from MP2 amplitudes. We extended this approach into an iterative scheme in which both the PNO's and the coefficients of the PNO's are iteratively refined [2]. We show the interplay between the truncation error and error attributed to suboptimal PNO's in an iterative PNO based nonlinear solver of the coupled cluster equations.

References

[1] J. Brabec, C. Yang, E. Epifanovsky, A.I. Krylov and E. Ng, *Reduced-cost sparsity-exploiting algorithm for solving coupled-cluster equations*, Journal of Computational Chemistry, **37** (2016), pp. 1059–1067.

[2] M. Clement, J. Zhang, C. A. Lewis, C. Yang and E. F. Valeev, *Assessment of Optimized Natural Orbitals for the Coupled Cluster Methods*, submitted, (2018).

[3] C. Edmiston and M. Krauss, *Pseudonatural Orbitals as a Basis for the Superposition of Configurations. I. He2+*, J. Chem. Phys., **45**, (1966), 1833.

[4] W. Meyer, *PNO–CI Studies of electron correlation effects. I. Configuration expansion by means of nonorthogonal orbitals, and application to the ground state and ionized states of methane*, J. Chem. Phys. **58**, (1973), 1017.

[5] F. Neese, F. Wennmohs and A. Hansen, *Efficient and accurate local approximations to coupled-electron pair approaches: An attempt to revive the pair natural orbital method.*, J. Chem. Phys., **130**, (2009), 114108.

Log-scaling tight-binding for material defects

Christoph Ortner

(joint work with Simon Etter)

Intuitively, there is very limited "information content" in the electronic structure of a localised defect embedded in a homogeneous medium, independent of or slowly growing with the medium's size. It should be possible to exploit this in order to develop highly efficient electronic structure methods for crystalline defects.

To formalise this idea, we consider a model, developed in [1, 2, 3, 4], for point defects and straight dislocation lines embedded in a homogeneous host crystal, taking into account both mechanical relaxation and electronic relaxation within the tight-binding model. For the sake of simplicity, this note will only describe the case of an impurity in $\mathbb{Z}^d$, with a 2-centre s-orbital tight-binding model.

More specifically, if $(y_\ell)_{\ell\in\Omega} \subset \mathbb{R}^d$ is a finite collection of atoms then we assume that a tight-binding hamiltonian is given by $H(y) = (h(r_{ij}))_{i,j\in\Omega}$ with $r_{ij} = |y_i - y_j|$ which is exponentially localised ($h(r) \lesssim e^{-\gamma r_{ij}}$ for some $\gamma > 0$). The potential energy landscape for the tight-binding model is then given by

$$E(y) = \sum_{s=1}^{N} f(\varepsilon_s), \qquad \text{where } H(y)\psi_s = \varepsilon_s\psi_s,$$

and $f(\varepsilon)$ is an analytic function describing either the canonical or grand-canonical ensemble for the electrons, see [3] for more detail.

It is then shown in [3, 2] that the problem of equilibrating $E(y)$ under suitable boundary conditions has a limit as the domain Ω approaches $\mathbb{Z}^d$ and that limit equilibrium displacements $\bar{u} : \mathbb{Z}^d \to \mathbb{R}^d$, $u = y - \mathrm{id}$ satisfy

$$\left|D^j \bar{u}(\ell)\right| \leq C_j |\ell|^{1-d-j} \tag{1}$$

where $Df(\ell) = (f(\ell + e_i) - f(\ell))_{i=1}^d$ denotes a discrete gradient operator. Indeed, we may expect (though it is an open problem whether this is true) that the stronger estimate

$$\left|D^j \bar{u}(\ell)\right| \leq C j! |\ell|^{1-d-j} \tag{2}$$

holds.

Our aim is to exploit this *a priori* known regularity of the equilibrium displacements to construct highly efficient numerical schemes for solving the electronic structure problem. To that end, as a first step, we establish an analogous regularity result for the density matrix, given in the finite domain case by

$$\Gamma := \sum_{s=1}^{N} f_{\mathrm{FD}}(\varepsilon_s)\, \psi_s \otimes \psi_s,$$

where f_{F} is the Fermi-Dirac function. In the thermodynamic limit it is more conveniently written as

$$\Gamma := \frac{1}{2\pi i} \oint f_{\mathrm{FD}}(z)(z - H)^{-1} dz,$$

where the integration is taken along a contour that circles the spectrum of $H(y)$ but does not circle any singularities of f_{FD}. Establishing regularity of electronic structure can be reduced to regularity of Γ and hence of $(z - H)^{-1}$. The following results use identities such as

$$D(z - H)^{-1} = -(z - H)^{-1}(DH)S(z - H)^{-1},$$

where $(S_{e_k} H)_{ij} = H_{i+e_k, j+e_k}$ and $D_{e_k} H = S_{e_k} H - H$, as well as Coombe-Thomas estimates (see [4] and references therein) to bound off-diagonal decay of $(z - H)^{-1}$.

The regularity (1) then implies that (unpublished)

$$\left|(D^k \Gamma)_{ij}\right| \leq C'_k e^{-\gamma'_k r_{ij}} \left(|i|^{1-d-k} + |j|^{1-d-k}\right).$$

Assuming the stronger regularity (2), we expect that (in preparation)

$$\left|(D^k \Gamma)_{ij}\right| \leq C k! e^{-\gamma r_{ij}} \left(|i|^{1-d-k} + |j|^{1-d-k}\right). \tag{3}$$

To exploit this regularity result, we propose to approximate each diagonal of the density matrix by a piece-wise polynomial (*hp*-FEM type approximation scheme). A little more precisely, if a uniform polynomial degree p is chosen and the finite element mesh size scales as $h(x) \sim |x|$, and is truncated at a suitable radius then under the regularity (1) it is relatively straightforward to establish a superalgebraic best-approximation rate

$$\|\Gamma - \Gamma_{\mathrm{hp}}\|_{\mathrm{F}} \leq C_t \mathrm{DOF}^{-t} \qquad \text{for all } t > 0.$$

It turns out, however, that standard (continuum) polynomial spectral approximation error estimates do not immediately apply in the discrete setting. We aim to establish that (3) implies

$$\|\Gamma - \Gamma_{\rm hp}\|_{\rm F} \leq C \exp\big(-c\mathrm{DOF}^{1/r}\big), \tag{4}$$

for some $c, r > 0$. Proving this result is work in progress, however, there is already overwhelming theoretical and numerical evidence for its validity.

The final ingredient, if (4) can be confirmed, is to develop an algorithm that efficiently computes $\Gamma_{\rm hp}$. A Galerkin discretisation for $\Gamma_{\rm hp}$ can achieve this in polynomial cost, which finally leads to a poly-logarithmic scaling result,

$$\mathrm{COST}\big(\Gamma_{\rm hp}\big) \lesssim \log^q\big(\|\Gamma - \Gamma_{\rm hp}\|_{\rm F}\big) \qquad \text{for some } q > 0.$$

References

[1] V. Ehrlacher, C. Ortner and A. V. Shapeev, *Analysis of Boundary Conditions for Crystal Defect Atomistic Simulations*, Arch. Ration. Mech. Anal., **222**, pp. 1217–1268, (2016). doi:10.1007/s00205-016-1019-6

[2] H. Chen, F. Q. Nazar and C. Ortner, *Geometry Equilibration of Crystalline Defects in Quantum and Atomistic Descriptions*, http://arxiv.org/abs/1709.02770, (2017).

[3] H. Chen, J. Lu and C. Ortner, *Thermodynamic Limit of Crystal Defects with Finite Temperature Tight Binding*, to appear in Arch. Ration. Mech. Anal.

[4] H. Chen and C. Ortner, *QM/MM Methods for Crystalline Defects. Part 1: Locality of the Tight Binding Model*, Multiscale Model. Simul., **14**, pp. 232–264, (2016). doi:10.1137/15M1022628

Current-density-functional theory for molecules in strong magnetic fields

Andrew M. Teale

(joint work with Tom J. P. Irons, James Furness, Erik I. Tellgren, Stella Stopkowicz and Trygve Helgaker)

Recent progress in the theoretical development and implementation of non-perturbative current-density-functional theory (CDFT) using London atomic orbitals is reviewed. These calculations enable study of chemical systems in strong magnetic fields up to $\sim$1 a.u. $\approx$ 235000 Tesla. Introducing a uniform magnetic field, $\mathbf{B} = \nabla \times \mathbf{A}$ described by a vector potential $\mathbf{A}$ leads to the electronic Hamiltonian

$$H(v, \mathbf{A}) = \frac{1}{2}\sum_i \mathbf{p}_i^2 + \sum_{i>j} |\mathbf{r}_i - \mathbf{r}_j|^{-1} + \sum_i v(\mathbf{r}_i) + \sum_i \mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i + \frac{1}{2}\sum_i \mathbf{A}^2(\mathbf{r}_i). \tag{1}$$

To setup the foundations of CDFT it is convenient to re-parameterize this Hamiltonian by collecting the scalar potential contributions as $u = v + \frac{1}{2}A^2$,

$$H(u, \mathbf{A}) = \frac{1}{2}\sum_i \mathbf{p}_i^2 + \sum_{i>j} |\mathbf{r}_i - \mathbf{r}_j|^{-1} + \sum_i u(\mathbf{r}_i) + \sum_i \mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i. \tag{2}$$

This has the convenient consequence that the energy $E(u, \mathbf{A})$ is concave in u and A (whereas $E(v, \mathbf{A})$ is not concave) and so a formulation of CDFT analogous to Lieb's formulation for DFT may be constructed [1].

A Kohn-Sham (KS) CDFT scheme can then be setup, with the KS equations,

$$\left[\frac{1}{2}p^2 + \frac{1}{2}\{\mathbf{p}, \mathbf{A}_\mathrm{s}\} + u_s + \mathbf{s}\cdot[\nabla \times \mathbf{A}_\mathrm{s}]\right]\varphi_p = \varepsilon_p \varphi_p \tag{3}$$

where the scalar potential and vector potentials are

$$u_\mathrm{s} = v_\mathrm{ext} + \frac{1}{2}A^2_\mathrm{ext} + v_\mathrm{J} + v_\mathrm{xc} \qquad \mathbf{A}_\mathrm{s} = \mathbf{A}_\mathrm{ext} + \mathbf{A}_\mathrm{xc}. \tag{4}$$

To provide an efficient computational implementation of CDFT we expand the KS orbitals in terms Gaussian type basis functions

$$\phi_a(\mathbf{r}) = (x - \mathrm{A}_x)^{a_x}(y - \mathrm{A}_y)^{a_y}(z - \mathrm{A}_z)^{a_z}\sum_{k=1}^{K_a} d_k e^{-\alpha_k|\mathbf{r}-\mathbf{A}|^2} \tag{5}$$

and attach a field dependent phase factor to yield London atomic orbitals (LAOs),

$$\omega_a(\mathbf{r}) = \phi_a(\mathbf{r}) e^{-\frac{i}{2}\mathbf{B}\times(\mathbf{A}-\mathbf{O})\cdot\mathbf{r}}. \tag{6}$$

The use of LAOs ensures gauge-origin independent energies are obtained.

In this talk we will examine two key aspects to allow the practical application of KS-CDFT; (i) techniques for the efficient evaluation of molecular integrals over LAOs, (ii) the nature of approximate exchange-correlation functionals in CDFT, benchmarking them against *ab initio* methods such as coupled-cluster theory [2]. Implementation of these methods in London [3] and Quest [4] is outlined.

Molecular Integrals

The most time consuming step in practical calculations is the evaluation of the electron repulsion integrals (ERIs) over the atomic orbitals. For LAOs the importance of this step in determining the efficiency of the calculations is magnified by the fact that complex arithmetic is required and the permutational symmetry is reduced from eightfold (for real orbitals) to fourfold (for the complex LAOs). The ERIs over the LAOs take the form

$$(\mathbf{ab}|\mathbf{cd}) = \iint \frac{\omega_a^*(\mathbf{r}_1)\omega_b(\mathbf{r}_1)\omega_c^*(\mathbf{r}_2)\omega_d(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{7}$$

and the most efficient implementations previously have used the McMurchie-Davidson approach. This approach gives recursions for the evaluation of the ERIs involving two-centre intermediates of the form (see Ref. [5] for details of notation),

$$\begin{aligned}[\mathbf{r} + \mathbf{1}_i]^{(\mathrm{m})} &= \mathbf{PQ}_i\,[\mathbf{r}]^{(\mathrm{m}+1)} + r_i\,[\mathbf{r} - \mathbf{1}_i]^{(\mathrm{m}+1)} \\ [\mathbf{p}|\mathbf{q}] \;\; &= (-1)^{\mathbf{q}}\,[\mathbf{p} + \mathbf{q}]^{(0)}\end{aligned} \tag{8}$$

when applied to Gaussian type atomic orbitals of the type in Eq. (5). When applied to LAOs these recursions are significantly more complicated,

$$\begin{aligned}[\mathbf{p}+\mathbf{1}_i|\mathbf{q}]^{(\mathrm{m})} =& -i\boldsymbol{\chi}_{\mathrm{P},i}\,[\mathbf{p}|\mathbf{q}]^{(\mathrm{m})} + \mathbf{PQ}_i\,[\mathbf{p}|\mathbf{q}]^{(\mathrm{m}+1)} \\ &+ p_i\,[\mathbf{p}-\mathbf{1}_i|\mathbf{q}]^{(\mathrm{m}+1)} - q_i\,[\mathbf{p}|\mathbf{q}-\mathbf{1}_i]^{(\mathrm{m}+1)}\end{aligned} \tag{9}$$

which leads to an intrinsic increase in computational cost of the McMurchie-Davidson scheme using LAOs. In both cases the four centre ERI is then constructed via the recursion

$$[\mathbf{a}+\mathbf{1}_i\,\mathbf{b}\,\mathbf{p}| = p_i\,[\mathbf{a}\,\mathbf{b}\,\mathbf{p}-\mathbf{1}_i| + \mathbf{PA}_i\,[\mathbf{a}\,\mathbf{b}\,\mathbf{p}| + \left(\frac{1}{2\zeta}\right)[\mathbf{a}\,\mathbf{b}\,\mathbf{p}+\mathbf{1}_i|\,. \tag{10}$$

This intrinsic increase in computational effort for the algorithm coupled with the need to calculate more integrals when dealing with LAOs has led us to consider other approaches to molecular integral evaluation.

Two of the most widely used schemes for evaluation of integrals over Gaussian-type atomic orbitals are the Head-Gordon-Pople (HGP) and Rys quadrature methods. For HGP the conventional recursion relations for the two-centre intermediates,

$$\begin{aligned}[\mathbf{e}+\mathbf{1}_i\mathbf{0}|\mathbf{f0}]^{(\mathrm{m})} =& \mathbf{PA}_i[\mathbf{e0}|\mathbf{f0}]^{(\mathrm{m})} - \mathbf{PQ}_i\left(\frac{1}{2\zeta}\right)[\mathbf{e0}|\mathbf{f0}]^{(\mathrm{m}+1)} \\ &+ e_i\left(\frac{1}{2\zeta}\right)\left\{[\mathbf{e}-\mathbf{1}_i\mathbf{0}|\mathbf{f0}]^{(\mathrm{m})} - \left(\frac{1}{2\zeta}\right)[\mathbf{e}-\mathbf{1}_i\mathbf{0}|\mathbf{f0}]^{(\mathrm{m}+1)}\right\} \\ &+ f_i\left(\frac{1}{2\zeta}\right)\left(\frac{1}{2\eta}\right)[\mathbf{e0}|\mathbf{f}-\mathbf{1}_i\mathbf{0}]^{(\mathrm{m}+1)}\end{aligned} \tag{11}$$

carry through essentially unaltered for LAOs, meaning that the intrinsic complexity of the algorithm is not increased. Four centre ERIs are then obtained via,

$$(\mathbf{ab}+\mathbf{1}_i| = (\mathbf{a}+\mathbf{1}_i\mathbf{b}| + \mathbf{AB}_i\,(\mathbf{ab}|\,. \tag{12}$$

For Rys quadrature the algorithm is also essentially unchanged (though the computation of the required roots and weights requires special care in the complex case—see Ref. [5]). In this scheme the integrands are determined recursively via

$$\begin{aligned}\mathcal{I}_i\,(e+1,f;\lambda) =& \left\{\mathbf{PA}_i - \frac{\eta t_\lambda^2}{\zeta+\eta}\mathbf{PQ}_i\right\}\mathcal{I}_i\,(e,f;\lambda) \\ &+\frac{e}{2\zeta}\left\{1-\frac{\eta t_\lambda^2}{\zeta+\eta}\right\}\mathcal{I}_i\,(e-1,f;\lambda) + \frac{f t_\lambda^2}{2(\zeta+\eta)}\mathcal{I}_i\,(e,f-1;\lambda)\end{aligned} \tag{13}$$

and then summed over the Rys nodes

$$[\mathbf{e0}|\mathbf{f0}] = \sum_{\lambda=1}^{N}\mathcal{I}_x\,(e_x,f_x;\lambda)\,\mathcal{I}_y\,(e_y,f_y;\lambda)\,\mathcal{I}_z\,(e_z,f_z;\lambda)\,w_\lambda \tag{14}$$

and the final four-centre ERI is recovered using the horizontal recursion relation employed in the HGP scheme.

As expected none of the above integral schemes is optimal for all types of ERI, in particular when integrals are classified according to their total angular momenta it becomes clear that the McMurchie-Davidson scheme remains most efficient for integrals over low angular momenta basis functions, whilst HGP is more efficient in the intermediate regime and Rys quadrature is most efficient for high angular momenta. I will discuss our recent implementation of a mixed scheme, illustrated in Fig. 1, in which the most appropriate algorithm is selected for each batch of integrals on the fly. The implementation of density-fitting (aka resolution of the identity) approaches will also be discussed.

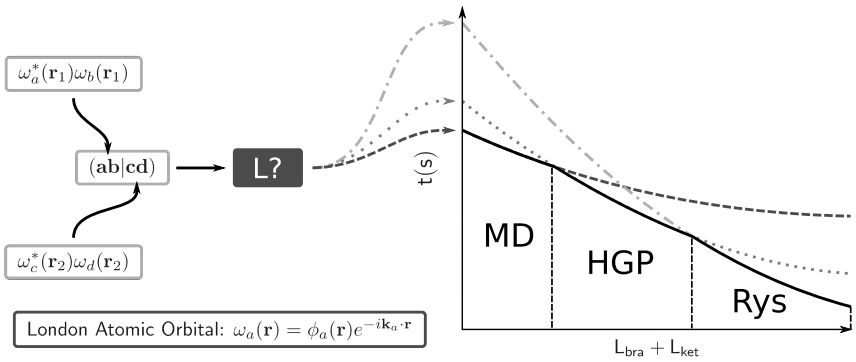


FIGURE 1. Schematic for selection of most appropriate integral evaluation scheme for LAO ERIs. The most efficient approach can be selected on-the-fly for batches of integrals classified according to their total angular momentum L.

EXCHANGE-CORRELATION FUNCTIONALS

The outstanding challenge for realization of a practical scheme for CDFT calculations is the development of appropriate exchange-correlation functionals depending on the paramagnetic current density,

$$\mathbf{j}_p = -\frac{i}{2}\sum_i [\phi_i^* \nabla\phi_i - \phi_i \nabla\phi_i^*]. \tag{15}$$

In previous work we have shown that simple vorticity based models fail catastrophically in strong magnetic fields [6]. However, we have recently demonstrated that meta-GGA class functionals, utilizing a modified kinetic energy density,

$$\tau \implies \tilde{\tau} = \tau - \frac{|\mathbf{j}_p|^2}{\rho}, \tag{16}$$

show remarkably accurate performance in strong magnetic fields in comparison with high accuracy coupled-cluster results [7]. I will discuss how this performance

can be rationalized by considering the importance of 1-electron regions and visualized by an extended [8] definition of the electron localization function (ELF)

$$f_{\mathrm{ELF}}(\mathbf{r}) = \frac{1}{1+\alpha(\mathbf{r})^2}, \qquad \alpha(\mathbf{r}) = \frac{[\tau(\mathbf{r}) - \tau^{\mathrm{vW}}(\mathbf{r})]}{\tau^{\mathrm{UEG}}(\mathbf{r})} \tag{17}$$

with $\tau^{\mathrm{vW}}(\mathbf{r})$ and $\tau^{\mathrm{UEG}}(\mathbf{r})$ the von Weisäcker and uniform electron gas definitions of the kinetic energy density, respectively. Finally, I will outline some outstanding challenges for CDFT calculations, including the accurate description of weak-field properties of general chemical interest such as nuclear magnetic resonance shielding constants [9] and the description of high spin ground states, which become prevalent as the strength of the magnetic field considered increases.

References

[1] E. I. Tellgren, S. Kvaal, E. Sagvolden, U. Ekström, A. M. Teale and T. Helgaker, *Choice of basic variables in current-density-functional theory*, Phys. Rev. A, **86** (2012), 062506.

[2] S. Stopkowicz, J. Gauss, K. K. Lange, E. I. Tellgren and T. Helgaker, *Coupled-cluster theory for atoms and molecules in strong magnetic fields*, J. Chem. Phys., **143** (2015), 074110.

[3] LONDON, a quantum-chemistry program for plane-wave/GTO hybrid basis sets and finite magnetic field calculations. By E. Tellgren (primary author), T. Helgaker, A. Soncini, K. K. Lange, A. M. Teale, U. Ekström, S. Stopkowicz, J. H. Austad and S. Sen. See `londonprogram.org` for more information.

[4] QUEST, a rapid development platform for Quantum Electronic Structure Techniques, 2017, `http://quest.codes`

[5] T. J. P. Irons, J. Zemen and A. M. Teale, *Efficient Calculation of Molecular Integrals over London Atomic Orbitals*, J. Chem. Theory Comput., **13** (2017), 2598.

[6] E. I. Tellgren, A. M. Teale, J. W. Furness, K. K. Lange, U. Ekström and T. Helgaker, *Non-perturbative calculation of molecular magnetic properties within current-density functional theory*, J. Chem. Phys., **140** (2014) 034101.

[7] J. W. Furness, J. Verbeke, E. I. Tellgren, S. Stopkowicz, U. Ekström, T. Helgaker and A. M. Teale, Current Density-Functional Theory using meta-Generalized Gradient Exchange-Correlation Functionals, J. Chem. Theory Comput., **11** (2015), 4169.

[8] J. W. Furness, U. Ekström, T. Hegaker and A. M. Teale, *Electron localisation function in current-density-functional theory*, Mol. Phys., **114** (2016), 1415.

[9] S. Reimann, U. Ekström, S. Stopkowicz, A. M. Teale, A. Borgoo, T. Helgaker, *The importance of current contributions to shielding constants in density-functional theory*, Phys. Chem. Chem. Phys., **17** (2015), 18834.

Wannier functions for metals

Antoine Levitt
(joint work with Horia Cornean, Anil Damle, David Gontier, Lin Lin and Domenico Monaco)

This talk summarized a recent effort towards the understanding of the localization properties of Wannier functions for metals [1, 2].

Wannier functions are a way to represent effectively the occupied subspace Span P where $P = \mathbb{1}(H \leq \varepsilon_F)$ is the spectral projector of a crystal in the independent electron approximation $H = -\frac{1}{2}\Delta + V_{\text{per}}$, where V_{per} is a d-dimensional periodic potential. By the Bloch theorem, this subspace is spanned by a set of Bloch functions, delocalized on the whole crystal. Wannier functions are a recombination of these Bloch functions to yield a set of localized functions that, together with their translates along the crystal lattice, form an orthogonal basis of the subspace. This is useful in applications to examine chemical bonding, interpolate band structures and speed up computations of exchange-correlation functionals [4].

By a Fourier-type duality, it is equivalent to find localized Wannier functions and to find a smooth and orthogonal basis of Span P_k, where $P_k = \mathbb{1}(H_k \leq \varepsilon_F)$, H_k are the Bloch-Floquet fibers of H, and k runs on the Brillouin zone $\mathcal{B}$, a set having the topology of a d-dimensional torus. For an insulator, there is a gap at the Fermi level ε_F, and P_k is smooth as a function of k, and the existence of localized Wannier is well-known to be equivalent to the triviality of the fiber bundle Span P_k.

For metals, P_k is not smooth as a function of k, and no localized Wannier functions in the classical sense can exist. However, a generalization of the concept is widely used in practice: instead of looking for an orthogonal basis of Span P, one looks instead for a larger set of orthogonal functions that span Span P. This is useful in reproducing band structure information, for instance in the context of Wannier interpolation [4].

In [1], we prove the existence of such a set. The main difficulty is the local topology (Chern number) carried by eigenvalue crossings. The construction is made possible by the fact that the sum on the Brillouin zone of the local topological numbers must vanish, by a Poincaré-Hopf type argument. This implies the existence of almost-exponentially localized Wannier functions in the sense above for a large class of metals.

In [2], we present a careful numerical study of Wannier functions for the simplest metal, the free electron gas. We show that while almost-exponentially localized functions do exist, the most widely used method to find them (the maximally-localized Wannier functions scheme, see [4]) only yields poorly localized Wannier functions.

References

[1] H. Cornean, D. Gontier, A. Levitt and D. Monaco, *Localised Wannier functions in metallic systems*, submitted.

[2] A. Damle, A. Levitt and L. Lin, *Variational formulation for Wannier functions with entangled band structure*, submitted.

[3] G. Panati, *Triviality of Bloch and Bloch-Dirac bundles*, Annales Henri Poincaré, (2007).

[4] N. Marzari, A. Mostofi, J. R. Yates, I. Souza and D. Vanderbilt, *Maximally localized Wannier functions: Theory and applications*, Rev. Mod. Phys., (2012).

Numerical methods for Brillouin zone integration

David Gontier

(joint work with Eric Cancès, Virginie Ehrlacher, Antoine Levitt and Damiano Lombardi)

In condensed matter, when studying numerically a periodic crystal, one needs to integrate some quantities over the Brillouin zone (a torus) $\mathbb{T}$. This is the case for the *integrated density of states*, of the form $\mathcal{N}(\varepsilon) := \int_{\mathbb{T}} \mathbf{1}(\varepsilon(k) \leq \varepsilon) dk$, where $\varepsilon(\cdot)$ is a given smooth function over $\mathbb{T}$, and for the *energy per unit cell*, of the form $E := \int_{\mathbb{T}} \varepsilon(k) \mathbf{1}(\varepsilon(k) \leq \varepsilon_F) dk$, where ε_F is the *Fermi level*, solution to $\mathcal{N}(\varepsilon_F) = N$, where N is a given number of electrons per unit cell.

In this talk, we discussed the different numerical methods that have been proposed to discretise numerically these integrals. The main difficulty is that the error on the energy E depends not only on the discretisation, but also on the error made on the Fermi level ε_F, which itself depends on the error on the integrated density of states $\mathcal{N}(\cdot)$.

In the case of insulators (existence of a spectral gap), we can rewrite the energy as the integral of a periodic smooth function. In this case, the approximation of the integral with a Riemann sum is enough to obtain an exponential rate of convergence with respect to the number of discretisation points (see e.g. [1]).

In the case of metallic systems, the convergence is much slower, and two families of methods have been proposed. In *interpolation methods*, we interpolate the (smooth) function $\varepsilon(\cdot)$, and we compute the quantities of interest from the interpolation. In *smearing methods*, we replace the discontinuous step function $\mathbf{1}$ by a smooth one, so that the integrand becomes smooth. In this talk, we presented the results of [2], where we provided the rates of convergence of these methods.

References

[1] D. Gontier and S. Lahbabi, *Convergence rates of supercell calculations in the reduced Hartree-Fock model*, M2AN (2016), pp. 1403–1424.

[2] É. Cancès, V. Ehrlacher, D. Gontier, A. Levitt and D. Lombardi, *Numerical Quadrature in the Brillouin zone for periodic Schrödinger operators*, in preparation.

A unified approach to Wannier interpolation

Anil Damle
(joint work with Lin Lin)

The construction of localized representations of electronic wavefunctions have a wide range of applications across quantum physics, material science, and chemistry. This is known as the Wannier localization problem, and the desired localized representations are known as Wannier functions [22, 13, 2]. For insulating materials with isolated eigenvalues, the problem is well studied mathematically [13, 2, 18, 12, 3, 10, 9, 19, 20, 17, 4, 7, 5] and good methods exist for computing Wannier functions in this setting [16, 6].

In contrast, when the eigenvalues are not isolated and become *entangled* far less is known. This situation arises naturally when considering metallic systems, but is also in insulating systems when considering a selected range of valance bands or conduction bands. In this setting the problem is significantly more difficult. Construction of Wannier functions now requires both identifying a subspace that contains a localized basis and constructing such a basis. A common methodology in this scenario is a *disentanglement* procedure [21]. Via two successive optimization procedures a subspace is identified and then a localized basis is computed.

In this talk we propose a unified method to address this so-called Wannier localization problem for both the isolated and entangled cases. We avoid an explicit, initial disentanglement step and utilize a quasi-density matrix that "entangles" eigenfunctions of interest with the rest of them in a controlled manner. This allows us to simultaneously identify the desired subspace and construct the localized basis via a direct method, thereby avoiding any dependence on using a good initial guess. In the isolated setting, our approach reduces to the existing selected columns of the density matrix (SCDM) algorithm [6].

The key idea behind the SCDM methodology is the use of a column-pivoted QR factorization to select "good" columns of a density or quasi-density matrix from which the desired localized functions can be constructed directly. While the SCDM methodology extends cleanly from molecules to crystals, here we restrict our discussion to molecules for simplicity, though the crystal case will be addressed in the talk. Details of the generalization to crystals and corresponding numerical experiments may be found in the preprint [8] available online.

We consider a single particle theory such as Kohn-Sham density functional theory (KSDFT) [11, 14], where the electronic wavefunctions are given by the eigenfunctions of a self-adjoint Hamiltonian $\mathcal{H}$. We denote the eigenfunctions as $\{\psi_i(\mathbf{r})\}$ and are interested in those that satisfy

$$\mathcal{H}\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad \varepsilon_i \in \mathcal{I} \tag{1}$$

for some energy window $\mathcal{I}$ that indicates the eigenfunctions of interest. Mathematically, the Wannier localization problem corresponds to finding orthonormal and localized functions $\{w_j\}$ such that

$$\operatorname{span}\{\psi_j\}_{\varepsilon_i \in \mathcal{I}} \subseteq \mathcal{V}_w := \operatorname{span}\{w_j\}.$$

The functions $\{w_j\}$ are the desired Wannier functions. In this formulation, the aforementioned isolated case is characterized by an isolation condition

$$\inf_{\varepsilon_i \in \mathcal{I}, \varepsilon_{i'} \notin \mathcal{I}} |\varepsilon_i - \varepsilon_{i'}| > 0. \tag{2}$$

When (2) is violated, we consider the eigenvalues entangled.

In the entangled setting, we construct the SCDM matrix through the use of a quasi-density matrix

$$P = \sum_i |\psi_i\rangle f(\varepsilon_i) \langle \psi_i| = f(H), \tag{3}$$

for some smooth $f(\cdot)$ such that $\mathcal{I}$ is a subset of the support of f. The two most common scenarios for entangled eigenvalues corresponds to Wannier localization either below or around a certain energy level. In both cases we choose f to be large on the region of interest and smoothly decay to zero outside $\mathcal{I}$ in a controlled manner. While formally the sum is over all the eigenfunctions, we can choose f to decay rapidly (*e.g.* as a complementary error function or Gaussian). By choosing f as an indicator function on $\mathcal{I}$ we can recover the density matrix for an isolated system. Given a smooth f, the kernel of the quasi-density matrix $P(\mathbf{r}, \mathbf{r}')$ decays rapidly [1, 15].

Therefore, to find N_w Wannier functions we select the N_w "most representative" and well conditioned columns of P and use them to construct Wannier functions. Define $\mathcal{E} = \operatorname{diag}[\{\varepsilon_i\}] \in \mathbb{R}^{N \times N}$containing all eigenvalues such that $f(\varepsilon)$ is above some threshold and $\Psi \in \mathbb{C}^{N_g \times N}$ be the matrix containing the corresponding discretized eigenvectors.

Computing the column-pivoted QR factorization

$$(f(\mathcal{E})\Psi^*)\,\Pi = QR \tag{4}$$

we let $\mathcal{C} = \{\mathbf{r}_i\}_{i=1}^{N_w}$ denote the N_w spatial points associated with the N_w columns permuted to the front by Π. Defining $\Xi \in \mathbb{C}^{N \times N_w}$ with $\Xi_{i,i'} = f(\varepsilon_i)\psi_i^*(\mathbf{r}_{i'})$, if the singular values of Ξ are bounded away from zero $U = \Xi(\Xi^*\Xi)^{-\frac{1}{2}}$ allows us to construct Wannier functions as

$$w_i(\mathbf{r}) = \sum_{i'=1}^{N} \psi_{i'}(\mathbf{r}) U_{i',i} \tag{5}$$

for $i = i, \ldots, N_w$. In this setting $U \in \mathbb{C}^{N \times N_w}$ is a rectangular matrix with orthonormal columns refereed to as a gauge.

The locality of the Wannier functions is a consequence of the locality of the quasi-density matrix (or the density matrix in the isolated case). Therefore, this SCDM methodology is able to construct Wannier functions for a wide range of systems directly, without relying on a good initial guess for the localized orbitals. One particularly important application of these localized functions is for band-structure interpolation of crystals. Examples of SCDM constructed Wannier functions in this setting may be found in [8].

References

[1] M. Benzi, P. Boito and N. Razouk, *Decay properties of spectral projectors with applications to electronic structure*, SIAM Rev., **55** (2013), pp. 3–64.

[2] E. I. Blount, *Formalisms of band theory*, Solid State Phys., **13** (1962), pp. 305–373.

[3] C. Brouder, G. Panati, M. Calandra, C. Mourougane and N. Marzari, *Exponential localization of Wannier functions in insulators*, Phys. Rev. Lett., **98** (2007), p. 046402.

[4] E. Cancès, A. Levitt, G. Panati and G. Stoltz, *Robust determination of maximally-localized Wannier functions*, Phys. Rev. B, **95** (2017), p. 075114.

[5] A. Damle, L. Lin and L. Ying, *Computing localized representations of the kohn-sham subspace via randomization and refinement*, SIAM J. Sci. Comput., to appear.

[6] A. Damle, L. Lin and L. Ying, *Compressed representation of Kohn–Sham orbitals via selected columns of the density matrix*, J. Chem. Theory Comput., **11** (2015), pp. 1463–1469.

[7] A. Damle, L. Lin and L. Ying, *Scdm-k: Localized orbitals for solids via selected columns of the density matrix*, J. Comput. Phys., **334** (2017), pp. 1–15.

[8] A. Damle and L. Lin, *Disentanglement via entanglement: A unified method for wannier localization*, arXiv:1703.06958, (2017).

[9] W. E, T. Li and J. Lu, *Localized bases of eigensubspaces and operator compression*, Proc. Natl. Acad. Sci., **107** (2010), pp. 1273–1278.

[10] F. Gygi, *Compact representations of Kohn–Sham invariant subspaces*, Phys. Rev. Lett., **102** (2009), p. 166406.

[11] P. Hohenberg and W. Kohn, *Inhomogeneous electron gas*, Phys. Rev., **136** (1964), pp. B864–B871.

[12] E. Koch and S. Goedecker, *Locality properties and Wannier functions for interacting systems*, Solid State Commun., **119** (2001), p. 105.

[13] W. Kohn, *Analytic properties of Bloch waves and Wannier functions*, Phys. Rev., 115 (1959), p. 809.

[14] W. Kohn and L. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev., **140** (1965), pp. A1133–A1138.

[15] L. Lin, *Localized spectrum slicing*, Math. Comp., (in press).

[16] N. Marzari and D. Vanderbilt, *Maximally localized generalized Wannier functions for composite energy bands*, Phys. Rev. B, **56** (1997), p. 12847.

[17] J. I. Mustafa, S. Coh, M. L. Cohen and S. G. Louie, *Automated construction of maximally localized Wannier functions: Optimized projection functions method*, Phys. Rev. B, **92** (2015), p. 165134.

[18] G. Nenciu, *Dynamics of band electrons in electric and magnetic fields: rigorous justification of the effective hamiltonians*, Rev. Mod. Phys., **63** (1991), pp. 91–127.

[19] V. Ozoliņš, R. Lai, R. Caflisch and S. Osher, *Compressed modes for variational problems in mathematics and physics*, Proc. Natl. Acad. Sci., **110** (2013), pp. 18368–18373.

[20] G. Panati and A. Pisante, *Bloch bundles, Marzari-Vanderbilt functional and maximally localized Wannier functions*, Commun. Math. Phys., **322** (2013), pp. 835–875.

[21] I. Souza, N. Marzari and D. Vanderbilt, *Maximally localized wannier functions for entangled energy bands*, Phys. Rev. B, **65** (2001), p. 035109.

[22] G. H. Wannier, *The structure of electronic excitation levels in insulating crystals*, Phys. Rev., **52** (1937), p. 191.

Magnetic fields, convexity, and gauge invariance in density-functional theory

Erik I. Tellgren

Density-functional theory is one of the most widely used electronic structure methods. Electrons interacting with a magnetic field are beyond the scope of the standard formulation of the theory, but two appropriate extensions are available [1, 2]. A novel extension can be obtained by using a magnetic Maxwell-Schrödinger model as the point of departure [3]. This extension in some respects generalizes Lieb's seminal work on standard density-functional theory [4] and can be interpreted as a Moreau-Yosida regularization of a more conventional model.

Denote the external electrostatic potential by v and the external magnetic vector potential by $\mathbf{A}$. In atomic units, the standard Schrödinger Hamiltonian is given by

$$H(v, \mathbf{A}) = T(\mathbf{A}) + \sum_{l=1}^{N} v(\mathbf{r}_l) + W \tag{1}$$

where the kinetic energy and the electron-electron repulsion terms are given by

$$T(\mathbf{A}) = \frac{1}{2} \sum_{l=1}^{N} \big(-i\nabla_l + \mathbf{A}(\mathbf{r}_l) \big)^2 \quad \text{and} \quad W = \sum_{k<l}^{N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}. \tag{2}$$

Following Lieb [4], densities ρ and electrostatic potentials v are taken to belong to dual function spaces, with a pairing $(\rho|v) = \int \rho(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r}$. Specifically, $\rho \in X := L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$ and $v \in X^* := L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. A magnetic field $\mathbf{B} = \nabla \times \mathbf{A} \in L^2_{\text{div}}(\mathbb{R}^3)$ is taken to be a divergence free $L^2(\mathbb{R}^3)$ function. The space of magnetic vector potentials is defined via the Fourier transform $\hat{\mathbf{A}}$ as those potentials that satisfy $k^2 \hat{\mathbf{A}}(\mathbf{k}) \in L^2$. The Schrödinger ground state energy is obtained by minimization over all wave functions in a magnetic Sobolev space $\mathcal{H}_{\mathbf{A}}$ [5],

$$E(v, \mathbf{A}) = \inf_{\Psi \in \mathcal{H}_{\mathbf{A}}} \langle \Psi | H(v, \mathbf{A}) | \Psi \rangle, \tag{3}$$

Exploiting gauge invariance, $E(v, \mathbf{A}) = E(v, \mathbf{A} + \nabla\chi)$ for all suitable restricted χ, this energy can be reinterpreted as a function of $\mathbf{B}$. Moreover, the energy can be expressed as a nested minimization over densities ρ and those wave functions $\Psi \mapsto \rho$ that reproduce a given density,

$$E(v, \mathbf{B}) = \inf_{\rho \in X} \big((\rho|v) + F_{\text{GH}}(\rho, \mathbf{B}) \big), \tag{4}$$

with the Grayce-Harris functional given by

$$F_{\text{GH}}(\rho, \mathbf{B}) = \inf_{\Psi \mapsto \rho} \langle \Psi | H(0, \mathbf{A}) | \Psi \rangle, \tag{5}$$

The energy functional E is known to be concave in v, but neither convex nor concave in $\mathbf{B}$, and the formula above can be identified with a partial Legendre-Fenchel transformation of F_{GH} with respect to the first variable.

Now let $\boldsymbol{\alpha}$ be a vector potential that describes an internal magnetic field induced by the electrons. In the magnetic Maxwell-Schrödinger model, with the notation $\boldsymbol{\beta} = \nabla \times \boldsymbol{\alpha}$,

$$E_\mu(v, \mathbf{B}) = \inf_{\boldsymbol{\alpha}} \Big(\frac{\|\boldsymbol{\beta}\|^2}{2\mu} + \inf_{\Psi} \langle \Psi | H(v, \mathbf{A} + \boldsymbol{\alpha}) | \Psi \rangle \Big). \tag{6}$$

The first term is the self-energy of the internal magnetic field, $\mu > 0$ is a parameter with a physical interpretation as the magnetic permeability of vacuum, and the second term can be identified with the Schrödinger energy $E(v, \mathbf{B} + \boldsymbol{\beta})$. A change of variables $\mathbf{b} = \mathbf{B} + \boldsymbol{\beta}$ now yields

$$E_\mu(v, \mathbf{B}) = \inf_{\mathbf{b}} \Big(\frac{\|\mathbf{B} - \mathbf{b}\|^2}{2\mu} + E(v, \mathbf{b}) \Big), \tag{7}$$

which is a Moreau-Yosida regularization of the Schrödinger energy $E(v, \mathbf{B})$ with respect to $\mathbf{B}$ [6, 7]. It can be remarked that this regularization is most natural to perform on a convex function, whereas $E(v, \cdot)$ is non-convex. Nonetheless, the regularization is beneficial in that it produces a paraconcave ("concave to within a square") energy functional. More specifically, using Eq. (4) above, one finds

$$\bar{E}_\mu(v, \mathbf{B}) := E_\mu(v, \mathbf{B}) - \frac{\|\mathbf{B}\|^2}{2\mu} = \inf_{\rho, \mathbf{b}} \Big((\rho | v) - \frac{(\mathbf{b}|\mathbf{B})}{\mu} + \frac{\|\mathbf{b}\|^2}{2\mu} + F_{\mathrm{GH}}(\rho, \mathbf{b}) \Big), \tag{8}$$

which is seen to be jointly concave in $(v, \mathbf{B})$. Save for the unconventional factor $-1/\mu$ (which can be eliminated by a change of variables $\mathbf{b}' = \mathbf{b}/\mu$), the above expression can be identified as a full Legendre-Fenchel transformation of the shifted Grayce-Harris functional $F(\rho, \mathbf{b}) = (2\mu)^{-1} \|\mathbf{b}\|^2 + F_{\mathrm{GH}}(\rho, \mathbf{b})$. I have not been able to establish that $F(\rho, \mathbf{b})$ is jointly convex. However, a full Legendre-Fenchel transformation of the concave $\bar{E}_\mu$ yields a functional

$$\bar{f}_\mu(\rho, \mathbf{b}) = \sup_{v, \mathbf{B}} \Big(\bar{E}_\mu(v, \mathbf{B}) - (\rho | v) + \frac{(\mathbf{b}|\mathbf{B})}{\mu} \Big) \tag{9}$$

that is jointly convex by construction and also a lower bound $\bar{f}_\mu(\rho, \mathbf{b}) \leq F(\rho, \mathbf{b})$. Eq. (8) remains valid when F is replaced by $\bar{f}_\mu$. Hence, the shifted ground state energy $\bar{E}_\mu(v, \mathbf{B})$ and the universal density functional $\bar{f}_\mu(\rho, \mathbf{b})$ constitute a pair of dual functionals that are each other's Legendre-Fenchel transform (with suitable sign conventions—Eqs. (8) and (9) involve minimization and maximization, respectively).

The interpretation in terms of regularization techniques can be taken further by introducing a second parameter $\lambda \leq \mu$ and defining the concave functional

$$\bar{E}_{\lambda\mu}(v, \mathbf{B}) = E_\mu(v, \mathbf{B}) - \frac{\|\mathbf{B}\|^2}{2\lambda} = E_\mu(v, \mathbf{B}) - \frac{\|\mathbf{B}\|^2}{2\mu} + \Big(\frac{1}{2\mu} - \frac{1}{2\lambda} \Big) \|\mathbf{B}\|^2. \tag{10}$$

The dual functional can be obtained as the full Legendre-Fenchel transformation

$$\bar{f}_{\lambda\mu}(\rho, \mathbf{b}) = \sup_{v, \mathbf{B}} \Big(\bar{E}_{\lambda\mu}(v, \mathbf{B}) - (\rho | v) + \frac{(\mathbf{b}|\mathbf{B})}{\lambda} \Big) = \sup_{v} \big(\bar{e}_{\lambda\mu}(v, \mathbf{b}) - (\rho | v) \big). \tag{11}$$

Here, a type of partial Legendre-Fenchel transformation with respect to the magnetic field has been introduced,

$$\bar{e}_{\lambda\mu}(v,\mathbf{b}) = \sup_{\mathbf{B}} \Big(\bar{E}_{\lambda\mu}(v,\mathbf{B}) + \frac{(\mathbf{b}|\mathbf{B})}{\lambda} \Big) = \frac{\|\mathbf{b}\|^2}{2\lambda} + \sup_{\mathbf{B}} \Big(E_\mu(v,\mathbf{B}) - \frac{\|\mathbf{B}-\mathbf{b}\|^2}{\lambda} \Big). \tag{12}$$

The last term is a Lasry-Lions regularization of E, given by a double Moreau-Yosida regularization of E, first as a minimization problem with parameter μ and second as a maximization problem with parameter λ. In the case of non-convex functions on Hilbert spaces, and parameters $\lambda < \mu$, this type of operation allows for stronger regularity results than simple Moreau-Yosida regularization [8, 9].

The formulation outlined above provides a gauge-invariant alternative to the Schrödinger-based convex formulation in Ref. [10], which featured the gauge dependent paramagnetic current density,

$$\mathbf{j}_\mathrm{p}(\mathbf{r}_1) = \mathrm{Im} \int \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)^* \nabla \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N, \tag{13}$$

as a variational parameter. The formulation also sheds light on attempts to formulate a density-functional theory that features the electron density ρ and the physical (gauge invariant) current density $\mathbf{j}$ as basic variables. (In the Schrödinger model, $\mathbf{j} = \mathbf{j}_\mathrm{p} + \rho\mathbf{A}$, and in the Maxwell-Schrödinger model, $\mathbf{j} = \mathbf{j}_\mathrm{p} + \rho(\mathbf{A} + \boldsymbol{\alpha})$.) There are strong indications that such formulations are not compatible with the standard variational principle [11]. In the present setting, this problem is circumvented in an instructive way. The total magnetic field $\mathbf{b} = \mathbf{B} + \boldsymbol{\beta}$ can be equivalently represented as a current density $\mathbf{k}$ that is *defined* to satisfy $\mu\mathbf{k} = -\nabla \times \mathbf{b}$. The current density $\mathbf{k}$ is an independent variational parameter, with no general connection to the electronic wave function. However, the minimizing wave function Ψ and $\boldsymbol{\alpha}$ in Eq. (6) are related—the stationarity condition reproduces a version of Ampere's law,

$$\mu\mathbf{k} = \mu\mathbf{j} - \nabla \times \mathbf{B}, \tag{14}$$

that relates a representation of the internal magnetic field ($\boldsymbol{\kappa}$) to the physical current density. Hence, while $\mathbf{j}$ is not suitable as a variational parameter, $\mathbf{k}$ can play this role and the two quantities agree to within $\mu^{-1}\nabla \times \mathbf{B}$ at the minimum.

References

[1] C. J. Grayce and R. A. Harris, *Magnetic-field density-functional theory*, Phys. Rev. A, **50** (1994), pp. 3089–3095.

[2] G. Vignale and M. Rasolt, *Density-functional theory in strong magnetic fields*, Phys. Rev. Lett., **59** (1987), pp. 2360–2363.

[3] E. I. Tellgren, *Density-functional theory for internal magnetic fields*, Phys. Rev. A, **97** (2018), 012504.

[4] E. H. Lieb, *Density functionals for Coulomb systems*, Int. J. Quantum Chem., **24** (1983), pp. 243–277.

[5] E. H. Lieb and M. Loss, *Analysis*, American Mathematical Society (2001).

[6] R. T. Rockafellar and R. J-B Wets, *Variational Analysis*, Springer (2009).

[7] S. Kvaal, U. Ekström, A. M. Teale and T. Helgaker, *Differentiable but exact formulation of density-functional theory*, J. Chem. Phys., **140** (2014), 18A518.

[8] J. M. Lasry and P. L. Lions, *A remark on regularization in Hilbert space*, Isr. J. Math. (1986), pp. 257–266.
[9] H. Attouch and D. Aze, *Approximation and regularization of arbitrary functions in Hilbert spaces by the Lasry-Lions method*, Ann. Inst. Henri Poincaré (1993), pp. 289–312.
[10] E. I. Tellgren, S. Kvaal, E. Sagvolden, U. Ekström, A. M. Teale and T. Helgaker, *Choice of basic variables in current-density-functional theory*, Phys. Rev. A (2012), 062506.
[11] A. Laestadius and M. Benedicks, *Nonexistence of a Hohenberg–Kohn variational principle in total current-density-functional theory*, Phys. Rev. A (2015), 032508.

The Future of the Electron-Correlation Problem: What about Full Configuration Interaction?

Jürgen Gauss
(joint work with Janus J. Eriksen)

The electron-correlation problem is at the heart of modern quantum chemistry, as its adequate treatment is essential for obtaining reliable and accurate results. While for so-called single-reference problems, i.e., cases where the wavefunction is well described by just a single Slater determinant, coupled-cluster theory has become the standard, a proper treatment of multireference cases still poses a challenge. To this day, a satisfactory formulation of a multireference extension of coupled-cluster theory still does not exist. The difficulties are here mainly due to the large set of requirements one tries to enforce, namely (1) size extensivity and consistency, (2) orbital invariance, (3) scaling of the cost independent of the size of the reference space, (4) proper number of parameters in the wavefunction ansatz, and (5) correct pole structure of the response function. Interest in multireference coupled-cluster theory is still high, but apparently there is currently a lack of new ideas.

A possible conclusion might be instead to seek for radically different solutions to the electron-correlation problem, in particular, for solutions that avoid the complexity of coupled-cluster theory. In this context, we suggest to aim directly at the full configuration-interaction (FCI) ansatz, which provides the exact solution of the correlation problem within a given one-electron basis set. By doing this, one avoids all issues concerning the list of formal requirements given above. With respect to the enormous computational cost of FCI, we suggest to solve the FCI problem only in a numerically approximate manner, i.e., with an accuracy of about 0.01 to 0.1 mHartree. Such an accuracy is sufficient for most applications in chemistry, as μHartree accuracy is rarely needed. In addition, we recommend to use simple algorithms, as this might significantly facilitate (massive) parallelization. The latter is today required in order to exploit the existing computing power.

There have actually been several suggestions for the solution of the electron-correlation problem along the lines given above, e.g., the density-matrix renormalization group approach, stochastic FCI, as well as various variants of incremental or selected (full) CI.

Our suggestion in this context is to use a many-body expansion (MBE) of the correlation energy [1]. This means that the FCI correlation energy E_{FCI} is

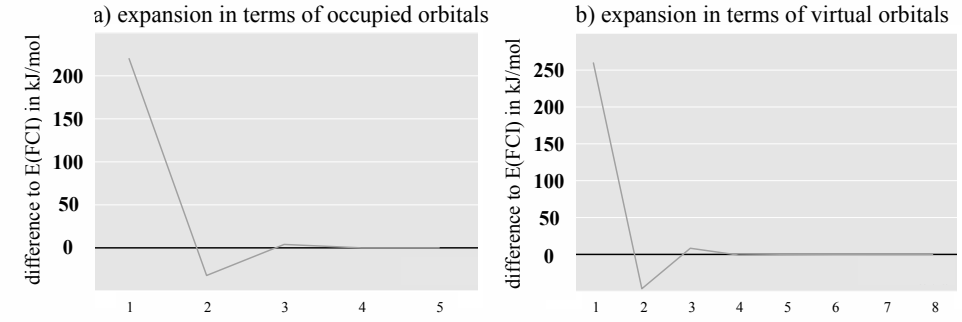
obtained as

$$E_{FCI} = \sum_{i}^{n_{occ}} \varepsilon_i + \sum_{i<j}^{n_{occ}} \Delta\varepsilon_{ij} + \sum_{i<j<k}^{n_{occ}} \Delta\varepsilon_{ijk} + \dots$$

where the first sum contains the correlation energies ε_i obtained with only one occupied spatial orbital correlated, the second sum accounts for corrections due to the simultaneous correlation of two occupied orbitals, the third for corrections due to the simultaneous correlation of three occupied orbitals, etc. The corrections are obtained in FCI calculations in which only the occupied orbitals referred to (indices $i, j, k, \dots$) are correlated together with the full set of virtual orbitals. This means that at the first level only up to double excitations appear in the FCI treatment, at the second level only up to quadruple excitations, etc. Our idea is not entirely new, as MBEs have often been used in quantum chemistry to treat large systems based on an expansion in terms of fragments. The MBE idea has also been used in the context of electron-correlation treatments; its first use goes back to work of Nesbet published in 1967.

While, as seen in Figure 1a, the so-called MBE-FCI scheme indeed provides convergence to the FCI limit, an MBE with respect to occupied orbitals has only

FIGURE 1. MBE-FCI results for water using a 6-31G basis set (H_2O, 13 basis functions) and expansions with respect to (a) occupied and (b) virtual orbitals.



a limited perspective, simply as the required individual FCI calculations with the full set of virtual orbitals are not feasible at higher orders. For this reason, we suggested in Ref. [1] to overcome this problem by instead performing an MBE with respect to virtual rather than occupied orbitals. In the corresponding expression for the FCI correlation energy the sums now runs over virtual orbitals and the individual calculations are carried out with all occupied orbitals included in the FCI treatment, but only a subset of virtual orbitals. Figure 1b demonstrates the convergence for the MBE-FCI expansion in terms of virtual orbitals.

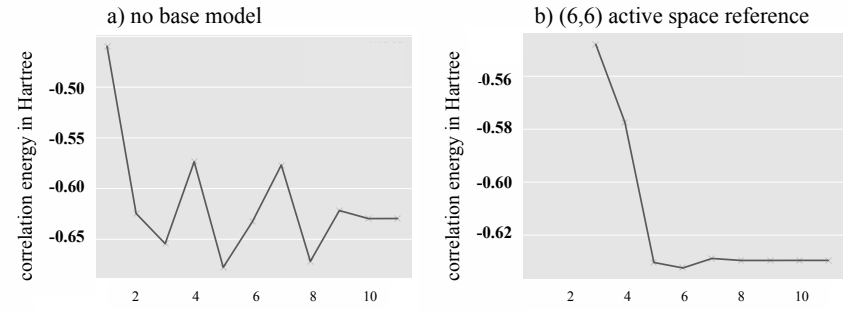
The MBE-FCI approach using an expansion in the virtual orbital space renders large-scale FCI-level treatments feasible (for first examples, see Ref. [1]). The price one has to pay for this is an exponential growth of the number of individual FCI computations that need to be carried out. However, this issue can be dealt with by

means of (1) a massive parallel implementation of the scheme and (2) an efficient screening protocol as described in Ref. [1].

Another idea to speed up our MBE-FCI treatment is to use a so-called base model. So far, the target energy has been the FCI correlation energy, but by introducing a base model (e.g., some approximate CC scheme), it is possible to target in the MBE only the difference in the correlation energies of FCI and the base model. As this is a much smaller quantity, convergence in the MBE is significantly faster.

Finally, we comment on the feasibility of MBE-FCI treatments for multireference problems. The version of MBE-FCI discussed so far is clearly biased towards a single Slater determinant as reference. For multireference cases, the convergence in the MBE is therefore slowed down or even erratic. A typical example is given in Figure 2a and shows the oscillations in the MBE-FCI treatment of a nitrogen mol-

FIGURE 2. MBE-FCI results for the nitrogen molecule using a 6-31G basis set (N_2, 18 basis functions) at twice the equilibrium distance using (a) no base model and (b) a (6,6) reference active space.



ecule (N_2) with an elongated bond distance. Our suggestion is here to introduce, in the spirit of other multireference treatments, a reference active space. This means that all occupied and active orbitals are always included in the individual calculations. The reference energy is now the so-called complete active space energy, the contributions at the leading level are obtained by doing FCI calculations with all occupied, all active, and one virtual orbital, the following level includes two virtual orbitals, etc. In practise this means that for multireference treatments, the leading level already includes higher than double excitations in the treatment, the following level higher than quadruple excitations, etc. One might consider this a disadvantage, but the expansion is now tailored to the problem and in this way fast convergence is ensured. Figure 2b shows how this multireference variant of our MBE-FCI scheme works for the stretched N_2 molecule when using a (6,6) active space as reference.

The MBE-FCI scheme with an expansion in the virtual orbital space is a rather new suggestion for FCI-level like treatments. It is a scheme designed for large-scale FCI calculations that aims at the same time at an accuracy of about 10^{-4}

Hartree or even better. First results presented in Ref. [1] as well as in forthcoming publications are very promising, but it is also clear that much further work is required to establish the MBE-FCI scheme as a routine tool in quantum chemistry.

References

[1] J. J. Eriksen, F. Lipparini and J. Gauss, *Virtual orbital many-body expansions: a possible route towards the full configuration interaction limit*, J. Phys. Chem. Lett., **8** (2017), pp. 4633–4639.

Hartree-Fock Excited States

Mathieu Lewin

The Hartree-Fock model is an important nonlinear approximation of the N-particle Schrödinger linear equation which describes the N electrons in an atom or a molecule. Its successes and limitations for approximating the first eigenfunction of the N-body Hamiltonian ("ground state") are well known, but its ability to describe excited states has probably been underestimated until recently. In a recent numerical work [1], a Hartree-Fock calculation has given very good predictions for 10 of the 11 first excited states of the H_2 molecule. These recent developments suggest that Hartree-Fock excited states need further mathematical and numerical investigation.

In the talk I have explained a recent result from [4] where I constructed infinitely many excited states for neutral and positively charged atoms and molecules, with energy levels below the first energy threshold (the lowest energy of the same system with one electron removed), and above the true Schrödinger eigenvalues.

To state the result, we introduce the N-particle operator describing the N electrons of a molecule

$$H(N) := -\sum_{j=1}^{N} \Delta_{x_j} - \sum_{j=1}^{N} \sum_{m=1}^{M} \frac{z_m}{|x_j - R_m|} + \sum_{1 \leq j < k \leq N} \frac{1}{|x_j - x_k|}$$

with domain $H^2_a((\mathbb{R}^3 \times \{\uparrow, \downarrow\})^N) \subset L^2_a((\mathbb{R}^3 \times \{\uparrow, \downarrow\})^N)$. The index a on H^2_a and L^2_a denotes the subspace of anti-symmetric functions, as is appropriate for fermions. A famous result of Zhislin and Sigalov [8, 9] asserts that when $N < \sum_{m=1}^{M} z_m + 1$, the operator $H(N)$ has infinitely many eigenvalues below its essential spectrum, denoted henceforth by $\lambda_k(H(N))$, $k \geq 1$.

In the Hartree-Fock model, the set of wavefunctions is restricted to the special class of Slater determinants

$$\Psi(x_1, \ldots, x_N) = \left(\sqrt{N!}\right)^{-1} \det(\phi_j(x_k))$$

where $\phi_1, \ldots, \phi_N$ is any orthonormal system in $L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\})$. We call $\mathcal{M}$ the manifold of these special states and

$$E_{\mathrm{HF}}(N) = \inf_{\Psi \in \mathcal{M}} \langle \Psi, H(N)\Psi \rangle$$

the corresponding minimal energy. Minimizers were shown to exist in [5, 7] for $N < \sum_{m=1}^{M} z_m + 1$ (neutral or positively charged molecules). Minimizers or other critical points of the quadratic form $\Psi \mapsto \langle \Psi, H(N)\Psi \rangle$ on $\mathcal{M}$ are found to solve the nonlinear coupled eigenvalue equations

$$(1) \quad \left(-\Delta - \sum_{m=1}^{M} \frac{z_m}{|R_m - x|} + \sum_{k=1}^{N} |\phi_k|^2 * \frac{1}{|\cdot|} \right) \phi_j - \sum_{k=1}^{N} \left((\phi_k \phi_j) * \frac{1}{|\cdot|} \right) \phi_k = \epsilon_j \, \phi_j$$

for $j = 1, \ldots, N$.

Theorem 1 (Hartree-Fock excited states)**.** *Assume that $N < \sum_{m=1}^{M} z_m + 1$. Then there exists infinitely many critical points $\Psi^{(k)}$ of the energy $\Psi \mapsto \langle \Psi, H(N)\Psi \rangle$ on the Hartree-Fock manifold $\mathcal{M}$, such that for all $k \geq 1$*

$$(2) \qquad \lambda_k(H(H)) \leq \langle \Psi^{(k)}, H(N)\Psi^{(k)} \rangle < E_{\mathrm{HF}}(N-1) < 0.$$

In a nonlinear theory such as Hartree-Fock, there is no clear equivalent of the essential spectrum. But it has been proved in [2, 3] that the lowest Hartree-Fock energy $E_{\mathrm{HF}}(N-1)$ of $N-1$ electrons satisfies similar mathematical properties as the bottom of an essential spectrum in the linear case, at least concerning the compactness of minimizing sequences. It is therefore natural to look for excited states with an energy below $E_{\mathrm{HF}}(N-1)$.

In [6, 7], Lions was the first to construct infinitely many Hartree-Fock excited states, but those have an energy converging to 0, which does not correspond to the picture of the Zhislin-Sigalov theorem. He used a min-max method in the space $H^1(\mathbb{R}^3 \times \{\uparrow, \downarrow\})^N$ of the N orbitals and Morse index bounds of min-maxing sequences to infer their compactness. His argument works the same for other similar nonlinear models, for instance when the exchange term (the last non-local term in (1)) is dropped.

In our proof of [4] we construct different critical points by working in the N-particle space. We therefore use that the Hartree-Fock model is obtained by restricting the true Schrödinger energy to the manifold $\mathcal{M}$ and our argument does not work for other similar nonlinear models. We use min-max techniques which can also be applied to the linear problem, and obtain thereby the variational inequality on the left of (2), by a simple comparison principle. We think our critical points are better candidates for representing molecular excited states since their energies converge to $E_{\mathrm{HF}}(N-1) < 0$ and not to 0. We did not use Morse index bounds to obtain the compactness of minimizing sequences, but actually proved that the Hartree-Fock energy satisfies the *Palais-Smale condition* below the first energy threshold $E_{\mathrm{HF}}(N-1)$, which allows us to use more classical techniques of nonlinear analysis. This is another property of Hartree-Fock theory which allows us to think of $E_{\mathrm{HF}}(N-1)$ as the bottom of a kind of nonlinear essential spectrum.

This research has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement MDFT No 725528).

References

[1] G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill, *Communication: Hartree-fock description of excited states of h2*, The Journal of Chemical Physics, **141** (2014), p. 111104.

[2] G. Friesecke, *The multiconfiguration equations for atoms and molecules: charge quantization and existence of solutions*, Arch. Ration. Mech. Anal., **169** (2003), pp. 35–71.

[3] M. Lewin, *Geometric methods for nonlinear many-body quantum systems*, J. Funct. Anal., **260** (2011), pp. 3535–3595.

[4] M. Lewin, *Existence of Hartree-Fock excited states for atoms and molecules*, Lett. Math. Phys., online first (2017).

[5] E. H. Lieb and B. Simon, *The Hartree-Fock theory for Coulomb systems*, Commun. Math. Phys., **53** (1977), pp. 185–194.

[6] P.-L. Lions, *Sur l'existence d'états excités dans la théorie de Hartree-Fock*, C. R. Acad. Sci. Paris Sér. I Math., **294** (1982), pp. 377–379.

[7] P.-L. Lions, *Solutions of Hartree-Fock equations for Coulomb systems*, Commun. Math. Phys., **109** (1987), pp. 33–97.

[8] G. M. Zhislin, *Discussion of the spectrum of Schrödinger operators for systems of many particles. (in Russian)*, Trudy Moskovskogo matematiceskogo obscestva, **9** (1960), pp. 81–120.

[9] G. M. Zhislin and A. G. Sigalov, *The spectrum of the energy operator for atoms with fixed nuclei on subspaces corresponding to irreducible representations of the group of permutations*, Izv. Akad. Nauk SSSR Ser. Mat., **29** (1965), pp. 835–860.

On the approximation of wavefunctions by anisotropic Gauss functions

Harry Yserentant

(joint work with Stephan Scholz)

The electronic Schrödinger equation describes the motion of N electrons under Coulomb interaction forces in a field of clamped nuclei. The solutions of this equation, the electronic wavefunctions, depend on $3N$ variables, three spatial dimensions for each electron. Approximating them is therefore inordinately challenging. I discussed the approximability of these wavefunctions by linear combinations of anisotropic Gauss functions, or more precisely Gauss-Hermite functions, products of polynomials and anisotropic Gauss functions in the narrow sense. Main result is that the original, singular wavefunctions can up to given accuracy and a negligibly small residual error be approximated with only insignificantly more such terms than their convolution with a Gaussian kernel of sufficiently small width and that basically arbitrary orders of convergence can be reached. This is a fairly surprising result, since it essentially means that by this type of approximation, the intricate hierarchies of non-smooth cusps in electronic wavefunctions have almost no impact on the convergence, once the global structure is resolved.

References

[1] St. Scholz and H. Yserentant, *On the approximation of electronic wavefunctions by anisotropic Gauss and Gauss-Hermite functions*, Numer. Math. **136**, pp. 841–874, 2017; also available as arXiv:1612.00360 [math.NA]

X2C as an effective Hamiltonian

Trond Saue

A starting point for relativistic molecular quantum mechanical calculations is the Dirac equation

$$\begin{bmatrix} V_{eN} + m_e c^2 & c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) & V_{eN} - m_e c^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} E, \tag{1}$$

where V_{eN} represents the interaction of electrons with the nuclear framework, c is the speed of light, m_e the mass of the electron, $\mathbf{p}$ the momentum operator and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is a vector collecting the Pauli spin matrices. The solutions are 4-component complex vector functions, with the upper two components collected as the large components ψ^L and the lower two collected as the small components ψ^S. A troublesome feature of the Dirac equation, as well as effective one-electron equations such as the 4-component relativistic Hartree-Fock or Kohn-Sham equation, is the presence of solutions of negative energy. Contrary to classical mechanics such solutions can not be ignored, since there is always a finite probability of energy jumps, even across gaps of energy of the order of $m_e c^2$.

A major breakthrough in the field of relativistic molecular calculations was the development of the exact 2-component relativistic Hamiltonian (X2C),[4, 7, 10, 11, 13, 8, 5, 15, 16, 17, 14] which reproduces *exactly* the positive energy spectrum of the 4-component parent Hamiltonian. It is obtained by block diagonalization of the parent Hamiltonian

$$U^\dagger \begin{bmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{bmatrix} U = \begin{bmatrix} h_{++} & 0 \\ 0 & h_{--} \end{bmatrix}. \tag{2}$$

In my contribution I point out that the X2C Hamiltonian is an example of an *effective Hamiltonian*, that is, that is an operator which reproduces *exactly* selected eigenvalues of the full Hamiltonian, but with *approximate* eigenvector restricted to a chosen model space. The machinery of effective Hamiltonians is nicely expressed in terms of principal angles and associated principal vectors relating the target space and the model space [6, 9].

I demonstrate that the X2C Hamiltonian is a canonical effective Hamiltonian[12] for which the effective eigenvectors are obtained by direct rotation of eigenvectors from the target space into the model space [18] under the constraint of least change [3]. An alternative 2-component relativistic Hamiltonian is obtained by the unnormalized elimination of the small component (UESC) [4]. This an example of a Bloch-Brandow effective Hamiltonian [1, 2]. In this case the effective eigenvectors are obtained by projection and the effective Hamiltonian is not self-adjoint.

References

[1] C. Bloch, *Sur la théorie des perturbations des états liés*, Nuc. Phys., **6**, pp. 329–347, 1958.
[2] B. H. Brandow, *Linked-Cluster Expansions for the Nuclear Many-Body Problem*, Rev. Mod. Phys., **39**, pp. 771–828, Oct 1967.
[3] L. S. Cederbaum, J. Schirmer and H. D. Meyer, *Block diagonalisation of Hermitian matrices*, J. Phys. A: Math. Gen., **22** (13), 2427, 1989.
[4] K. Dyall, *Interfacing relativistic and nonrelativistic methods. I. Normalized eliminiation of the small component in the modified Dirac equation*, J. Chem. Phys., **106**, 9618, 1997.
[5] M. Filatov and K. Dyall, *On convergence of the normalized elimination of the small component (NESC) method*, Theor. Chem. Acc., **117**, pp. 333–338, 2007.
[6] G. Golub and C. van Loan, *Matrix Computations*, Johns Hopkins, Baltimore, MD, 1989.
[7] M. Iliaš, H. J. Aa. Jensen, V. Kellö, B. O. Roos and M. Urban, *Theoretical study of PbO and the PbO anion*, Chem. Phys. Lett., **408**, 210, 2005.
[8] M. Iliaš and T. Saue, *An infinite-order two-component relativistic Hamiltonian by a simple one-step transformation*, J. Chem. Phys., **126**, 064102, 2007.
[9] A. V. Knyazev and M. E. Argentati, *Principal Angles between Subspaces in an A-Based Scalar Product: Algorithms and Perturbation Estimates*. SIAM Journal on Scientific Computing, **23** (6), pp. 2008–2040, 2002.
[10] W. Kutzelnigg and W. Liu, *Quasirelativistic theory equivalent to fully relativistic theory*, J. Chem. Phys., **123**, 241102, 2005.
[11] W. Kutzelnigg and W. Liu, *Quasirelativistic theory I. Theory in terms of a quasirelativistic operator*, Mol. Phys., **104**, pp. 2225–2240, 2006.
[12] S. Kvaal, *Geometry of effective hamiltonians*, Phys. Rev. C, **78**, 044330, Oct 2008.
[13] W. Liu and D. Peng, *Infinite-order quasirelativistic density functional method based on the exact matrix quasirelativistic theory*, J. Chem. Phys., **125**, 044102, 2006.
[14] W. Liu, *Advances in relativistic molecular quantum mechanics*, Phys. Rep., **537** (2), pp. 59–89, 2014.
[15] W. Liu and W. Kutzelnigg, *Quasirelativistic theory. II. Theory at matrix level*, J. Chem. Phys., **126**, 114107, 2007.
[16] W. Liu and D. Peng, *Exact two-component hamiltonians revisited*, J. Chem. Phys., **131**, 031104, 2009.
[17] T. Saue, *Relativistic Hamiltonians for Chemistry: A Primer*, Chem. Phys. Chem., **12**, 3077, 2011.
[18] J. H. Van Vleck, *On σ-type doubling and electron spin in the spectra of diatomic molecules*, Phys. Rev., **33**, pp. 467–506, Apr 1929.

An overview of *a posteriori* estimation and post-processing methods for nonlinear eigenvalue problems

Geneviève Dusson

(joint work with Eric Cancès, Yvon Maday, Benjamin Stamm and Martin Vohralík)

Many mathematical models aiming at the determination of electronic structures give rise to nonlinear eigenvalue problems. This is for example the case of the Hartree-Fock model and the Density Functional Theory (DFT) models (e.g. Kohn-Sham). Other nonlinear eigenvalue problems appear in different contexts, e.g. in nonlinear elasticity for the calculation of vibration modes of a mechanical structure, or the Gross-Pitaevskii equation which is used for the computation of the steady states of Bose-Einstein condensates.

Controlling the errors arising in the resolution of such problems, and especially the errors due to (i)—the chosen discretization, and (ii)—the algorithm used to solve the eigenvalue problem (mostly iterative methods) is essential for at least two reasons. First, it allows to guarantee the accuracy of the approximation, and therefore to complement the computed output with an error bar. Second, it enables an optimization of the parameters used in the simulation (e.g. the number of degrees of freedom versus the number of iterations) to reach a given accuracy at a minimal computational cost. The control of this error is usually done by means of *a posteriori* error estimates.

The main object of this work is to compare different error estimation methods for nonlinear eigenvalue problems in a unified framework. To do so, we consider the ground state of a generic relatively simple *nonlinear eigenvalue* problem arising from a minimization problem: Find $(u, \lambda) \in X \times \mathbb{R}$, such that $\|u\| = 1$ and

$$Au + g(u^2)u = \lambda u, \tag{1}$$

where A is a linear, bounded-below, self-adjoint operator on a separable Hilbert X with domain $D(A)$ and compact resolvent. In our applications, g depends on the electronic density ρ, which is equal to u^2 in the case of only one eigenfunction. We focus on the lowest eigenvalue λ of the problem.

A Galerkin discretization of this problem writes: Find $(u_{N_c}, \lambda_{N_c}) \in X_{N_c} \times \mathbb{R}$ with $\|u_{N_c}\| = 1$ such that

$$\forall v_{N_c} \in X_{N_c}, \quad \langle \left(A + g(u_{N_c}^2)\right) u_{N_c}, v_{N_c} \rangle = \lambda_{N_c} \langle u_{N_c}, v_{N_c} \rangle. \tag{2}$$

We compare and analyze here mainly four different works. These works provide error estimations for different linear and nonlinear eigenvalue problems. Note that these error estimations can be used in two different ways. They can be used to give a guaranteed bound on the error as explained above, but they can also be used to post-process the approximate solution, and therefore obtain a more accurate solution, hopefully at a low computational overcost.

We first consider the error estimation and post-processing performed for the Hartree-Fock equations in 2003 [5]. In this article, the authors present an error estimation as well as a post-processing step for the discrete solution of the Hartree-Fock problem, which relies on a second-order Taylor expansion of the energy.

Second, we present the *a posteriori* error estimation for the Gross-Pitaevskii equation presented in 2016 [4]. This estimation provides first a coarse guaranteed upper bound of the eigenvector error, based on a first-order Taylor expansion of the residual. The approach is then refined to propose a bound that is very close to the real error, valid only in the asymptotic regime where the error is small enough, but which can be checked in practice using the first guaranteed bound.

Third, we introduce the post-processing method based on perturbation theory for the Kohn-Sham equations [2, 3]. This method provides an improvement for the energy as well as the orbitals in the case of a planewave discretization of these equations that is very cheap to compute.

Finally, we mention the two-grid methods presented in 1999 for a linear eigenvalue problem [6], and in 2017 for a nonlinear eigenvalue problem [1]. In this

method, the full problem is solved on a coarse grid, and a boundary value problem (or a linear eigenvalue problem in the nonlinear case) is solved on a fine grid, to improve the solution on the coarse grid.

In each case, it is possible to relate the error estimation or the post-processing to a first-order Taylor expansion of the error. More precisely, let us denote the residual of the equation by F, i.e.

$$\forall v \in X,\ \forall \mu \in \mathbb{R}, \quad F(v,\mu) = Av + g(v^2)v - \mu v.$$

For the exact eigenpair $(u,\lambda) \in X \times \mathbb{R}$, there holds

$$F(u,\lambda) = Au + g(u^2)u - \lambda u = 0.$$

Writing a first-order development of the residual around the coarse eigenpair $(u_{N_c}, \lambda_{N_c}) \in X_{N_c} \times \mathbb{R}$, where X_{N_c} is the discretization space gives an approximation of the error at first order by

$$DF^{-1}_{(u_{N_c},\lambda_{N_c})} F(u_{N_c}, \lambda_{N_c}).$$

These different methods providing error estimations or post-processing for the energy and the eigenfunction can all be derived from some approximation of this equation. This leads to different computational overcosts, and different precisions of the error estimates or the post-processed quantities. Presenting these methods in a same framework can help the practitioner to better choose the method corresponding to his/her needs and constraints in terms of computational cost and required accuracy.

References

[1] E. Cancès, R. Chakir, L. He and Y. Maday, *Two-grid methods for a class of nonlinear elliptic eigenvalue problems*, IMA Journal of Numerical Analysis, **38** (2), pp. 605–645, 2017

[2] E. Cancès, G. Dusson, Y. Maday, B. Stamm M. Vohralík, *A perturbation-method-based a posteriori estimator for the planewave discretization of nonlinear Schrödinger equations*, Comptes Rendus Mathematique, **352** (11), pp. 941–946, 2014.

[3] E. Cancès, G. Dusson, Y. Maday, B. Stamm M. Vohralík, *A perturbation-method-based post-processing for the planewave discretization of Kohn–Sham models*, Journal of Computational Physics, **307**, pp. 446–459, 2016.

[4] G. Dusson and Y. Maday, *A posteriori analysis of a nonlinear Gross–Pitaevskii-type eigenvalue problem*, IMA Journal of Numerical Analysis, **37** (1), pp. 94–137, 2017.

[5] Y. Maday and G. Turinici, *Error bars and quadratically convergent methods for the numerical simulation of the Hartree-Fock equations*, Numerische Mathematik, **94** (4), pp. 739–770, 2003.

[6] J. Xu and A. Zhou, *A two-grid discretization scheme for eigenvalue problems*, Mathematics of Computation, **70** (233), pp. 17–26, 1999.

Density of states for optical spectra of molecules by low-rank approximation

Boris Khoromskij

(joint work with Peter Benner, Venera Khoromskaia, Sergey Dolgov and Chao Yang)

The breaking through approach to low-parametric representation of multivariate functions and operators is based on the principle of separation of variables which can be realized by using nonlinear approximation in rank-structured tensor formats like canonical, Tucker and tensor train (TT) representations. The method of quantized TT (QTT) approximation is proven to provide the logarithmic data-compression on a wide class of discretized functions and operators [8]. The new range-separated tensor format [2] allows the efficient rank-structured representation of non-regular many-particle interaction potentials and scattered data. Thus bridging of the modern multilinear algebra and the nonlinear approximation theory allows to construct the novel tensor numerical methods with the linear complexity scaling in dimension, hence breaking the "curse of dimensionality" [9].

In this talk we provide the short introduction to tensor numerical methods and and briefly overview the most commonly used tensor formats.

We then discuss how to construct the rank-structured tensor approximation of the basic two-electron integrals (TEI) tensor in the Hartree-Fock calculation [6] and in MP2 techniques [7], see the survey paper [12] on the related literature. The fourth order TEI tensor, $\mathbf{B} = [b_{\mu\nu\kappa\lambda}]$, is defined in the form

$$b_{\mu\nu\kappa\lambda} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{g_\mu(x)g_\nu(x)g_\kappa(y)g_\lambda(y)}{\|x-y\|}dxdy, \tag{1}$$

where the size N_b of the basis set $\{g_\mu\}$, $\mu = 1, \ldots, N_b$ (say, Gaussian type orbitals), chosen for approximating the Hartree-Fock equation, may vary from several tens to several hundreds and even larger. The large $N_b^2 \times N_b^2$ TEI matrix B is approximated in the form of rank-R_B decomposition [6, 7]

$$B := [b_{\mu\nu,\kappa\lambda}] \approx LL^T, \quad \text{with} \quad L \in \mathbb{R}^{N_b^2 \times R_B},\ R_B \sim N_b,$$

by using the truncated Cholesky decomposition of B with on-the-fly computation of the required column vectors $B(:, j^*) = \sum_{k=1}^{R} \odot_{\ell=1}^{3} V^{(\ell)} M_k^{(\ell)} V^{(\ell)}(:, j^*)^T$. The latter is performed by using the precomputed factorization of B via the 1D "density fitting" scheme.

We describe the reduced basis approach to the Bethe-Salpeter equation (BSE) (spectral problem describing excitation energies of molecules) introduced in [1]. The 2×2-block representation of the BSE system matrix leads to the following eigenvalue problem,

$$H\begin{pmatrix}\mathbf{x}_k\\ \mathbf{y}_k\end{pmatrix} \equiv \begin{pmatrix}A & B\\ -B^* & -A^*\end{pmatrix}\begin{pmatrix}\mathbf{x}_k\\ \mathbf{y}_k\end{pmatrix} = \omega_k \begin{pmatrix}\mathbf{x}_k\\ \mathbf{y}_k\end{pmatrix}, \tag{2}$$

where the matrix blocks of size $n \times n$ with $n = O(N_b^2)$ are defined by

$$A = \mathbf{\Delta\varepsilon} + V - \widehat{W}, \quad B = V - \widetilde{W}, \tag{3}$$

and eigenvalues ω_k correspond to the excitation energies. Here $\mathbf{\Delta\varepsilon}$ is a diagonal matrix and $V = [v_{ia,jb}]$ is the rank-R_B TEI matrix $B \approx LL^T$ projected onto the Hartree-Fock molecular orbital basis [7, 1]. Matrices $\widehat{W}$ and $\widetilde{W}$ can be constructed by using certain transforms of V.

Our approach is based on the diagonal plus low-rank approximation of the matrix blocks A and B in BSE system matrix (by using some results in [11]) inherited from the low-rank Cholesky factorization of the TEI matrix in the molecular orbitals basis [7]. The structured eigenvalue solver, based on the use of the Sherman-Morrison-Wudbury formula for rank-structured representation of the matrix inverse, allows to accurately calculate several eigenvalues in the central part of the spectrum with the linear cost in the matrix size. The enhanced algorithm applies to the improved block-diagonal plus low-rank structure in the BSE matrix [1, 3]. The QTT tensor approximation of the matrix blocks allows to solve the partial structured eigenvalue problem in the logarithmic cost with respect to the large matrix size [3].

Finally, we present a new method to efficiently and accurately approximate the density of states (DOS) for large rank-structured matrices [4] with application to the diagonal block A in the BSE matrix (the so-called Tamm-Duncoff approximation). We use the simple definition of the DOS for symmetric matrices

$$\phi(t) = \frac{1}{n}\sum_{j=1}^{n} \delta(t - \lambda_j), \quad t, \lambda_j \in [0, a], \tag{4}$$

where δ is the Dirac delta and the λ_j's are the eigenvalues of $A = A^T$ ordered as $\lambda_1 \le \lambda_2 \le \cdots \le \lambda_n$. The traditional methods for approximation of the DOS function [10], based on a polynomial or fractional-polynomial interpolation of the DOS regularized by Gaussians or Lorentzians, and computing traces of matrix resolvents, defined at a large set of interpolation points, are hardly applicable to the complicated spectral data of the large BSE system. Our approach is based on Lorentzian blurring, i.e. replacing each Dirac-δ by a Lorentzian,

$$\delta(t) \rightsquigarrow L_\eta(t) := \frac{1}{\pi}\frac{\eta}{t^2 + \eta^2} = \frac{1}{\pi}\mathrm{Im}\left(\frac{1}{t - i\eta}\right), \tag{5}$$

so that an approximate DOS can be written as

$$\phi(t) \approx \phi_\eta(t) := \frac{1}{n}\sum_{j=1}^{n} L_\eta(t - \lambda_j). \tag{6}$$

The regularized DOS takes the form

$$\phi(t) \approx \phi_\eta(t) := \frac{1}{n\pi}\sum_{j=1}^{n} \mathrm{Im}\left(\frac{1}{(t - \lambda_j) - i\eta}\right) = \frac{1}{n\pi}\mathrm{Im}\,\mathrm{Trace}[(tI - A - i\eta I)^{-1}], \tag{7}$$

or keeping real-valued arithmetics,

$$\phi_\eta(t) := \frac{1}{n\pi}\sum_{j=1}^{n}\frac{\eta}{(t-\lambda_j)^2+\eta^2} = \frac{1}{n\pi}\mathrm{Trace}[((tI-A)^2+\eta^2 I)^{-1}]. \tag{8}$$

In both cases the task of computing the approximate DOS $\phi_\eta(t)$ reduces to approximating the trace of the matrix resolvent

$$(tI - A - i\eta I)^{-1} \quad \text{or} \quad ((tI-A)^2+\eta^2 I)^{-1}.$$

Our method amounts to estimating the DOS by evaluating traces of the matrix resolvent represented in the block-diagonal plus low-rank form (the Sherman-Morrison-Wudbury formula). The main contribution is to perform each function evaluation at low cost and to reduce the total number of function evaluations to $O(\log N)$ in the case of fine representation grid of size $N \gg n$ by using the QTT tensor interpolation via the adaptive cross approximation.

The efficiency of presented tensor methods is illustrated by numerical examples.

References

[1] P. Benner, V. Khoromskaia and B. N. Khoromskij, *A reduced basis approach for calculation of the Bethe-Salpeter excitation energies using low-rank tensor factorizations*, Molecular Physics, **114** (7–8), pp. 1148–1161, 2016.

[2] P. Benner, V. Khoromskaia and B. N. Khoromskij, *Range-separated tensor formats for numerical modeling of many-particle interaction potentials*, SIAM J. Sci. Comput., **40** (2), pp. A1034–A1062, 2018.

[3] P. Benner, S. Dolgov, V. Khoromskaia and B. N. Khoromskij, *Fast iterative solution of the Bethe-Salpeter eigenvalue problem using low-rank and QTT tensor approximation*, J. Comp. Phys., **334**, pp. 221–239, 2017.

[4] P. Benner, V. Khoromskaia, B. N. Khoromskij and C. Yang, *Computing the density of states for optical spectra by low-rank and QTT tensor approximation*, available as e-preprint: arXiv:1801.03852, 2018.

[5] V. Khoromskaia and B. N. Khoromskij, *Tensor Numerical Methods in Quantum Chemistry: from Hartree-Fock to Excitation Energies*, Phys. Chemistry Chem. Physics, 2015, **17**, pp. 31491–31509.

[6] V. Khoromskaia, B. N. Khoromskij and R. Schneider, *Tensor-structured calculation of two-electron integrals in a general basis*, SIAM J. Sci. Comput., **35** (2), 2013, pp. A987–A1010.

[7] V. Khoromskaia and B. N. Khoromskij, *Møller-Plesset (MP2) Energy Correction Using Tensor Factorizations of the Grid-based Two-electron Integrals*, Comp. Phys. Comm., **185**, pp. 2–10, 2014.

[8] B. N. Khoromskij, *$O(d\log N)$-Quantics Approximation of N-d Tensors in High-Dimensional Numerical Modeling*, J. Constr. Approx. v. **34** (2), pp. 257–289 (2011).

[9] B. N. Khoromskij, *Tensor Numerical Methods in Scientific Computing*, Research monograph, De Gruyter Verlag, Berlin, 2018.

[10] L. Lin, Y. Saad and C. Yang, *Approximating spectral densities of large matrices*, SIAM Review, **58** (1), pp. 34–65, 2016.

[11] E. Rebolini, J. Toulouse and A. Savin, *Electronic excitation energies of molecular systems from the Bethe-Salpeter equation: Example of H_2 molecule*, in: Concepts and Methods in Modern Theoretical Chemistry (S. Ghosh and P. Chattaraj eds), vol 1: Electronic Structure and Reactivity, p. 367, 2013.
[12] S. Reine, T. Helgaker and R. Lindh, *Multi-electron integrals*, WIREs Comput. Mol. Sci. **2**, pp. 290–303 (2012).

A Quadratic Error Estimate for the Coupled-Cluster Method Tailored by Tensor Network States

Fabian M. Faulstich
(joint work with Andre Laestadius, Simen Kvaal, Örs Legeza and Reinhold Schneider)

The tailored Coupled-Cluster (TCC) method [4] is based on a very appealing ansatz, namely, the so-called *split amplitude* ansatz [6, 7, 1, 8]. Here, a CAS-FCI computation is performed on a subsystem yielding the solution ψ_{CAS}. This solution is then *dynamically corrected*, e.g., the CCSD scheme is such a correction capturing the dynamical correlation on the external system. Using this approach we are able to avoid the conventional MRCC methods and all their difficulties, but are still able to compute multi-configuration systems.

A sever drawback of the TCC method is that it is based on the single-reference CC theory. Consequently, to cover the system's static correlations we need a large CAS space, which scales exponentially in its dimensionality, i.e., it suffers from the curse of dimensionality. A correction to this was only recently achieved by approximating the FCI solution via the density matrix renormalization group (DMRG) method [13, 14], a high accuracy tool to compute static correlation, which fails, however, for dynamical correlation [14, 2].

Before presenting the TCC-energy error analysis performed in [3], we introduce the TCC method in a formal way:

We start by defining the basis splitting for the considered N-electron problem. Let $\{\chi_1, \dots, \chi_K\} \subseteq H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ be a set of $L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$-orthonormal spin orbitals with $K > N$ and ϕ_0 be the considered reference Slater determinant. We define

$$\mathscr{B}_{\mathrm{CAS}} = \{\underbrace{\chi_1, \dots, \chi_N}_{\text{occupied}}, \underbrace{\chi_{N+1}, \dots, \chi_k}_{\text{unoccupied}}\}\,, \quad \mathscr{B}_{\mathrm{ext}} = \{\underbrace{\chi_{k+1}, \dots, \chi_K}_{\text{external}}\}$$

and furthermore $\mathcal{B}_{\mathrm{CAS}} = \{\phi[\mu_1, \dots, \mu_N] : \mu_i \in \{1, \dots, k\}, \mu_1 < \dots < \mu_N\}$. The corresponding FCI space $\mathcal{H}_{\mathrm{CAS}}$ is then defined as the span of $\mathcal{B}_{\mathrm{CAS}}$. Analogously, we split the set of excitation-indices $\mathcal{J}$ describing the set of possible excitations, i.e., $\mathcal{J}_{\mathrm{CAS}} = \{\mu \in \mathcal{J} : X_\mu \phi_0 \in \mathcal{H}_{\mathrm{CAS}}\}$ and $\mathcal{J}_{\mathrm{ext}} = \{\mu \in \mathcal{J} : X_\mu \phi_0 \notin \mathcal{H}_{\mathrm{CAS}}\}$. An important observation is that $\mathcal{J}_{\mathrm{ext}}$ does not only contain excitations into states purely excited in $\mathscr{B}_{\mathrm{ext}}$ but also into mixed states, i.e., for the virtual orbitals $\mathrm{v}(\mu) = (A_1, \dots, A_r)$ of the excitation index μ, there exists at least one $l \in \{1, \dots, r\}$ such that $A_l \in \{k+1, \dots, K\}$. Note that the dynamic correction will note capture static correlation, hence, we need $\mathcal{H}_{\mathrm{CAS}}$ to contain all

of the system's static correlation. Subsequently, we describe how this is ensured by using concepts from the field of quantum information theory. Let U be a low-rank DMRG solution on the FCI space $\mathcal{H}_K$ represented in the TT-format [5]. From this solution we compute the one particle and two particle densities $\mathbf{D}[i] = \mathbf{U}[i]^T\mathbf{U}[i]$ and $\mathbf{D}[i,j] = \mathbf{U}[i,j]^T\mathbf{U}[i,j]$, where the matrisization $\mathbf{U}[i] \in \mathbb{R}^{2^{K-1}\times 2}$ is defined by $U[i]_{(\mathsf{m}_1,\ldots,\not{\mathsf{m}}_i,\ldots,\mathsf{m}_K),(\mathsf{m}_i)}$ and $\mathbf{U}[i,j] \in \mathbb{R}^{2^{K-2}\times 4}$ is defined by $U[i,j]_{(\mathsf{m}_1,\ldots,\not{\mathsf{m}}_i,\ldots,\not{\mathsf{m}}_j,\ldots,\mathsf{m}_K)(\mathsf{m}_i,\mathsf{m}_j)}$. From these densities we compute the mutual information $I(i,j) = s(i) + s(j) - s(i,j)$, where s denotes the to $\mathbf{D}[i]$ resp. $\mathbf{D}[i,j]$ corresponding *Von Neumann entropy*, i.e., $s(i) = -\mathrm{Tr}(\mathbf{D}[i]\ln\mathbf{D}[i])$ resp. $s(i,j) = -\mathrm{Tr}(\mathbf{D}[i,j]\ln\mathbf{D}[i,j])$. For a more detailed description of the connection between these quantum information theory concepts and electronic structure theory, we refer the reader to [11, 12]. To describe the TCC method by means of a non-linear Galerkin scheme we consider K, $N \in \mathbb{N}$ with $K > N$ to be fixed, $\mathscr{B} = \{\chi_1,\ldots,\chi_K\}$ to be a set of $L^2(\mathbb{R}^3\times\{\pm\frac{1}{2}\})$-orthonormal spin orbitals and ϕ_0 a reference state for an N-electron problem. Further, we assume $\mathscr{B}_{\mathrm{CAS}}$ and $\mathscr{B}_{\mathrm{ext}}$ to be a partition of $\mathscr{B}$ and $\phi_{\mathrm{CAS}} = e^{T^{\mathrm{CAS}}}\phi_0$ to be the FCI approximation on the complete active space $\mathcal{H}_{\mathrm{CAS}}$. We define the TCC function $f(\,\cdot\,;t^{\mathrm{CAS}}) : \mathcal{V}_{\mathrm{ext}} \to \big(\mathcal{V}_{\mathrm{ext}}\big)'$ with $t \mapsto f(t;t^{\mathrm{CAS}})$, where for $\mu \in \mathcal{J}_{\mathrm{ext}}$

$$\begin{aligned}\big(f(t;t^{\mathrm{CAS}})\big)_\mu &= \langle\phi_\mu, e^{-T^{\mathrm{CAS}}}e^{-T}He^{T}e^{T^{\mathrm{CAS}}}\phi_0\rangle \\ &= \langle\phi_\mu, e^{-T^{\mathrm{CAS}}}\exp(-\sum_{\nu\in\mathcal{J}_{\mathrm{ext}}} t_\nu X_\nu)H\exp(\sum_{\nu\in\mathcal{J}_{\mathrm{ext}}} t_\nu X_\nu)e^{T^{\mathrm{CAS}}}\phi_0\rangle\ .\end{aligned}$$

In addition, let the TCC-energy functional be given by

$$\mathcal{E}(t;t^{\mathrm{CAS}}) = \langle\phi_0, e^{-T^{\mathrm{CAS}}}e^{-T}He^{T}e^{T^{\mathrm{CAS}}}\phi_0\rangle\ .$$

We now give a short descriptive summary of the energy-error analysis given in [3]. As a non-variational method, it is not immediate that the TCC method has a quadratic energy error bound. Besides deriving such a bound we subsequently present an error analysis solving the following three problems:

First, note that the TCC method does not specify what method shall be used on $\mathcal{H}_{\mathrm{CAS}}$ to compute ψ_{CAS}. For the sake of generality, we therefore want to derive an error bound that explicitly contains the error on $\mathcal{H}_{\mathrm{CAS}}$, i.e.,

$$\Delta E_{\mathrm{CAS}} = |\langle\phi_0, \big(e^{-T^{\mathrm{CAS}}}PHPe^{T^{\mathrm{CAS}}} - e^{-T_{\mathrm{FCI}}^{\mathrm{CAS}}}PHPe^{T_{\mathrm{FCI}}^{\mathrm{CAS}}}\big)\phi_0\rangle|\ .$$

Second, we recall that for the single-reference CC method a quadratic error bound was derived by Schneider and Rohwedder [10, 9]. A major difference to the analysis presented in these articles is that we can not assume a HOMO-LUMO gap, as we are considering multi-configuration systems. Consequently, the in [10, 9] presented analysis needs to be generalized to the here considered case of a CAS-ext gap, i.e., $\varepsilon_0 = \lambda_{k+1} - \lambda_k > 0$ where $\{\lambda_k\}$ denotes the spectrum of the Fock operator. Third, the TCC method will in general not converge to the FCI limit. This is due to its basis-splitting nature and shall be reflected in the energy-error bound.

For the energy-error analysis let $\mathscr{B} = \{\chi_1,\ldots,\chi_K\}$ be a set of spin orbitals that are split into $\mathscr{B}_{\mathrm{CAS}}$ and $\mathscr{B}_{\mathrm{ext}}$. We denote $\mathcal{H}_K$ and $\mathcal{H}_{\mathrm{CAS}}$ the FCI space

corresponding to $\mathscr{B}$ resp. $\mathscr{B}_{\mathrm{CAS}}$. Further, $t_*^{\mathrm{CAS}} \in \mathcal{V}_{\mathrm{CAS}}$ corresponds to the FCI solution on $\mathcal{H}_K$ projected on $\mathcal{H}_{\mathrm{CAS}}$, $t_{\mathrm{FCI}}^{\mathrm{CAS}} \in \mathcal{V}_{\mathrm{CAS}}$ the FCI solution on $\mathcal{H}_{\mathrm{CAS}}$, and $t^{\mathrm{CAS}} \in \mathcal{V}_{\mathrm{CAS}}$ an approximation to $t_{\mathrm{FCI}}^{\mathrm{CAS}}$. Let $\mathcal{V}_{\mathrm{ext}}^{(d)} \subset \mathcal{V}_{\mathrm{ext}}$ be a subspace fulfilling

$$d(t_*, \mathcal{V}_{\mathrm{ext}}^{(d)}) \leq \frac{\gamma\delta}{\gamma + L},$$

where $\gamma, L > 0$ are the monotonicity and Lipschitz constants of $f(\,\cdot\,; t^{\mathrm{CAS}})$ on $B_\delta(t_*)$. This corresponds to $\mathcal{V}_{\mathrm{ext}}^{(d)}$ being a *sufficiently* good approximation space. Then there exists a unique solution $t_d \in \mathcal{V}_{\mathrm{ext}}^{(d)}$ of $f(\,\cdot\,; t^{\mathrm{CAS}})|_{\mathcal{V}_{\mathrm{ext}}^{(d)}} = 0$ that approximates the solution $t_* \in \mathcal{V}_{\mathrm{ext}}$ of $f(\,\cdot\,; t^{\mathrm{CAS}}) = 0$ on $\mathcal{V}_{\mathrm{ext}}$. Let $(z_d, z_*) \in \mathcal{V}_{\mathrm{ext}}^{(d)} \times \mathcal{V}_{\mathrm{ext}}$ be the corresponding dual solutions of $(t_d, t_*) \in \mathcal{V}_{\mathrm{ext}}^{(d)} \times \mathcal{V}_{\mathrm{ext}}$. Further, set $\tilde{t}_* \in \mathcal{V}_{\mathrm{ext}}$ the solution of $f(\,\cdot\,; t_{\mathrm{FCI}}^{\mathrm{CAS}}) = 0$ on $\mathcal{V}_{\mathrm{ext}}$ and $t_*^{\mathrm{ext}} \in \mathcal{V}_{\mathrm{ext}}$ the projection of the FCI solution on $\mathcal{H}_K$ onto $\mathcal{H}_{\mathrm{CAS}}^{\perp}$. We now split the energy error

$$\begin{aligned}
\Delta E &= |\mathcal{E}(t_d; t^{\mathrm{CAS}}) - \mathcal{E}(t_*^{\mathrm{ext}}; t_*^{\mathrm{CAS}})| \\
&\leq \underbrace{|\mathcal{E}(t_d; t^{\mathrm{CAS}}) - \mathcal{E}(t_*; t^{\mathrm{CAS}})|}_{=\Delta\varepsilon} + \underbrace{|\mathcal{E}(t_*; t^{\mathrm{CAS}}) - \mathcal{E}(t_*; t_{\mathrm{FCI}}^{\mathrm{CAS}})|}_{=\Delta\varepsilon_{\mathrm{CAS}}} \\
&\quad + \underbrace{|\mathcal{E}(t_*; t_{\mathrm{FCI}}^{\mathrm{CAS}}) - \mathcal{E}(t_*^{\mathrm{ext}}; t_*^{\mathrm{CAS}})|}_{=\Delta\varepsilon_{\mathrm{CAS}}^*}
\end{aligned}$$

and derive upper bounds for each of the above 'sub-errors', i.e., $\Delta\varepsilon$, $\Delta\varepsilon_{\mathrm{CAS}}$ and $\Delta\varepsilon_{\mathrm{CAS}}^*$. By using a Taylor expansion and the fact that $(t_*^{\mathrm{ext}}, t_*^{\mathrm{CAS}})$ is a stationary point of the energy functional $\mathcal{E}$, we find (cf. Lemma 26 in [3])

$$\begin{aligned}
\Delta\varepsilon_{\mathrm{CAS}}^* &= |\mathcal{E}(t_*; t_{\mathrm{FCI}}^{\mathrm{CAS}}) - \mathcal{E}(t_*^{\mathrm{ext}}; t_*^{\mathrm{CAS}})| \lesssim \|t_* - t_*^{\mathrm{ext}}\|_{\mathcal{V}_{\mathrm{ext}}}^2 + \|t_{\mathrm{FCI}}^{\mathrm{CAS}} - t_*^{\mathrm{CAS}}\|_2^2 \\
&\quad \left(\lesssim \|t_* - \tilde{t}_*\|_{\mathcal{V}_{\mathrm{ext}}}^2 + \|\tilde{t}_* - t_*^{\mathrm{ext}}\|_{\mathcal{V}_{\mathrm{ext}}}^2 + \|t_{\mathrm{FCI}}^{\mathrm{CAS}} - t_*^{\mathrm{CAS}}\|_2^2 \right) .
\end{aligned}$$

Furthermore, we can recast ΔE_{CAS}, the energy error on $\mathcal{H}_{\mathrm{CAS}}$ from the error expression $\Delta\varepsilon_{\mathrm{CAS}}$. We find (cf. Lemma 27 in [3])

$$\begin{aligned}
\Delta\varepsilon_{\mathrm{CAS}} &= |\mathcal{E}(t_*; t^{\mathrm{CAS}}) - \mathcal{E}(t_*; t_{\mathrm{FCI}}^{\mathrm{CAS}})| \\
&\lesssim \Delta E_{\mathrm{CAS}} + \|t_* - \tilde{t}_*\|_{\mathcal{V}_{\mathrm{ext}}}^2 + \|(T^{\mathrm{CAS}} - T_{\mathrm{FCI}}^{\mathrm{CAS}})\phi_0\|_{H^1}^2 + \sum_{|\mu|=1} \varepsilon_\mu(\tilde{t}_*)_\mu^2 .
\end{aligned}$$

Finally, it is straight forward to generalize the analysis presented in [10, 9] to hold for the above introduced CAS-ext gap assumption (cf. [3]). This yields

$$\begin{aligned}
\Delta\varepsilon &= |\mathcal{E}(t_d; t^{\mathrm{CAS}}) - \mathcal{E}(t_*; t^{\mathrm{CAS}})| \\
&\lesssim \|t_d - t_*\|_{\mathcal{V}_{\mathrm{ext}}} \left(\|t_d - t_*\|_{\mathcal{V}_{\mathrm{ext}}} + \|z_d - z_*\|_{\mathcal{V}_{\mathrm{ext}}} \right) .
\end{aligned}$$

Combining these estimates we obtain the following energy-error bound for the TCC method

$$\Delta E \lesssim \|t_d - t_*\|_{\mathcal{V}_{\text{ext}}} \left(\|t_d - t_*\|_{\mathcal{V}_{\text{ext}}} + \|z_d - z_*\|_{\mathcal{V}_{\text{ext}}}\right) + \|t_* - t_*^{\text{ext}}\|_{\mathcal{V}_{\text{ext}}}^2 + \|t_* - \tilde{t}_*\|_{\mathcal{V}_{\text{ext}}}^2 + \|t_{\text{FCI}}^{\text{CAS}} - t_*^{\text{CAS}}\|_2^2 + \|t^{\text{CAS}} - t_{\text{FCI}}^{\text{CAS}}\|_2^2 + \sum_{\substack{\mu \in \mathcal{J}_{\text{ext}} \\ |\mu|=1}} \varepsilon_\mu (\tilde{t}_*)_\mu^2 + \Delta E_{\text{CAS}} \ .$$

We see that if ΔE_{CAS} posses a quadratic error bound and the $\{\tilde{t}_*\}$ amplitudes for single excitations are small, then we have a quadratic energy-error bound. For TNS-TCC methods we have such a quadratic bound for ΔE_{CAS} as the used tensor optimization algorithms are variational. Furthermore, we can assume without loss generality that the $\{\tilde{t}_*\}$ amplitudes for single excitations are small, as a rotation into Brueckner orbitals ensures this property. Hence, TNS-TCC methods have the same asymptotic behavior as CI schemes.

References

[1] L. Adamowicz, P. Piecuch and K. B. Ghose, *The state-selective coupled cluster method for quasi-degenerate electronic states*, Molecular Physics, (1998), pp. 225–234.

[2] G. K.-L. Chan and S. Sharma, *The Density Matrix Renormalization Group in Quantum Chemistry*, Annual Review of Physical Chemistry, (2011), pp. 465–481.

[3] F. M. Faulstich, A. Laestadius, S. Kvaal, Ö. Legeza and R. Schneider, *Analysis of The Coupled-Cluster Method Tailored by Tensor-Network States in Quantum Chemistry*, arXiv:1802.05699 [math.NA].

[4] H. O. Kinoshita and R. J. Bartlett, *Coupled-cluster method tailored by configuration interaction*, The Journal of chemical physics **123** (7), (2005), 074106.

[5] I. V. Oseledets, *Tensor-train decomposition*, SIAM Journal on Scientific Computing (2011), pp. 2295–2317.

[6] P. Piecuch, N. Oliphant and L. Adamowicz, *A state selective multireference coupled cluster theory employing the single reference formalism*, The Journal of chemical physics, (1993), pp. 1875–1900.

[7] P. Piecuch and L. Adamowicz, *State-Selective Multireference Coupled-Cluster Theory Employing the Single-Reference Formalism: Implementation and Application to the H8 Model System*, The Journal of chemical physics, (1994), pp. 5792–5809.

[8] P. Piecuch, *Active-space coupled-cluster methods*, Molecular Physics, (2010), pp. 2987.-3015.

[9] T. Rohwedder and R. Schneider, *Error estimates for the Coupled Cluster method*, ESAIM: Mathematical Modelling and Numerical Analysis, (2013).

[10] R. Schneider, *Analysis of the projected coupled cluster method in electronic structure calculation*, Numerische Mathematik, **113** (3), (2009), pp. 433–471.

[11] S. Szalay, G. Barcza, T. Szilvási, L. Veis and Ö. Legeza, *The correlation theory of the chemical bond*, Scientific Reports, **7**, (2016).

[12] *S. Szalay et al.*, *Tensor product methods and entanglement optimization for ab initio quantum chemistry*, International Journal of Quantum Chemistry, (2015), pp. 1342–1391.

[13] L. Veis, A. Antalík, J. Brabec, F. Neese, Ö. Legeza and J. Pittner, *Coupled cluster method with single and double excitations tailored by matrix product state wave functions*, The journal of physical chemistry letters, **7** (20), (2016), pp. 4072–4078.

[14] L. Veis, A. Antalík, Ö. Legeza, A. Alavi and J. Pittner, *Full Configuration Interaction Quantum Monte Carlo Benchmark and Multireference Coupled Cluster Studies of Tetramethyleneethane Diradical*, arXiv:1801.01057 [physics.chem-ph].

Singular Analysis of Coupled Cluster Equations and its Implication for Simulation

Heinz-Jürgen Flad
(joint work with Gohar Flad-Harutyunyan)

Modern *first principles* quantum chemistry relies to a large extend on models which make no explicit use of many-particle wavefunctions but instead are based on reduced quantities like density matrices, Green's and response functions. For a system of particles interacting via singular Coulomb potentials these reduced quantities show a specific singular behaviour near diagonals. Whereas much effort has been spend to understand the singular behaviour of many-particle wavefunctions, cf. [8] much less is known about reduced quantities. We have started a research project to study the asymptotic properties of reduced quantities within the framework of *coupled cluster* (CC) theory, cf. [1]. This particular many-particle theory is presently considered as the ultimate benchmark in quantum chemistry. Despite its practical significance, a rigorous mathematical analysis of CC models is still in its infancy, see however recent progress on the subject by Schneider, Rohwedder, Kvaal and Laestadius [10, 12, 13, 14]. In order to achieve a detailed understanding of the reduced quantities mentioned before, it is first of all necessary to study the asymptotic behaviour of reduced pair and possibly higher order amplitudes which constitute the CC wavefunction via the exponential ansatz. This is the subject of the present work with focus on nonlinear CC models within the random phase approximation (RPA). Solutions of these models are commonly represented by series of a particular class of Goldstone diagrams so-called RPA diagrams. In Ref. [7], we presented a detailed asymptotic analysis of these RPA diagrams using techniques from singular analysis. In particular, we provided a connection between RPA diagrams and classical pseudo-differential operators which enables an efficient treatment of the linear and nonlinear interactions in these models.

In order to give a brief outline of the problem and how we handled it, let us discuss a highly simplified nonlinear model problem for a pair amplitude $\tau(\mathbf{x}_1, \mathbf{x}_2)$, where $\mathbf{x}_1, \mathbf{x}_2 \in \mathbb{R}^3$ denote the coordinates of an electron pair. This model contains various linear interaction terms of the pair amplitude given by

$$f_{V^{(2)}\tau}(\mathbf{x}_1, \mathbf{x}_2) := V^{(2)}(\mathbf{x}_1, \mathbf{x}_2)\, \tau(\mathbf{x}_1, \mathbf{x}_2), \quad f_{V^{(1)}\tau}(\mathbf{x}_1, \mathbf{x}_2) := V^{(1)}(\mathbf{x}_1)\, \tau(\mathbf{x}_1, \mathbf{x}_2),$$

$$f_{V^{(2)}\circ\tau}(\mathbf{x}_1, \mathbf{x}_2) := \int V^{(2)}(\mathbf{x}_1, \mathbf{x}_3)\, \tau(\mathbf{x}_3, \mathbf{x}_2)\, d\mathbf{x}_3$$

and a nonlinear term of the form

$$f_{\tau\circ V^{(2)}\circ\tau}(\mathbf{x}_1, \mathbf{x}_2) := \int \tau(\mathbf{x}_1, \mathbf{x}_3) V^{(2)}(\mathbf{x}_3, \mathbf{x}_4) \tau(\mathbf{x}_4, \mathbf{x}_2)\, d\mathbf{x}_3 d\mathbf{x}_4$$

where $V^{(1)}$, $V^{(2)}$ correspond to one and two-particle interactions, respectively. The basic structure of the model can be represented by the nonlinear equation

$$A\tau = -V^{(2)} - f_{V^{(2)}\tau} + f_{V^{(1)}\tau} - f_{V^{(2)}\circ\tau} - f_{\tau\circ V^{(2)}\circ\tau}. \tag{1}$$

where A is an elliptic second order partial differential operator.

It is common practice in quantum chemistry to solve (1) via a fixed point iteration scheme. First one solves the equation $A\tau_0 = -V^{(2)}$ with fixed right hand side. Calculate $f_{V^{(2)}\tau_0}$, $f_{V^{(1)}\tau_0}$, $f_{V^{(2)}\circ\tau_0}$ and $f_{\tau_0\circ V^{(2)}\circ\tau_0}$ and in the next iteration step one solves

$$A\tau_1 = -V^{(2)} - f_{V^{(2)}\tau_0} + f_{V^{(1)}\tau_0} - f_{V^{(2)}\circ\tau_0} - f_{\tau_0\circ V^{(2)}\circ\tau_0}. \tag{2}$$

The last two steps can be repeated generating a iterative sequence of linear equations

$$A\tau_{n+1} = -V^{(2)} - f_{V^{(2)}\tau_n} + f_{V^{(1)}\tau_n} - f_{V^{(2)}\circ\tau_n} - f_{\tau_n\circ V^{(2)}\circ\tau_n}. \tag{3}$$

which are solved in a consecutive manner until convergence of the sequence $\tau_1, \tau_2, \tau_3, \ldots$ has been achieved. In [7], we were mainly interested in the asymptotic behaviour of iterated pair amplitudes τ_i, $i = 0, 1, \ldots$, near coalescence points of electrons. In order to extract these properties we applied methods from singular analysis [2, 9, 15] and solved (3) via an explicitly constructed asymptotic parametrix and corresponding Green operator, cf. [3, 4, 5, 6] for further details. In order to deal with the (non) linear interactions on the right hand side, we employed operator algebraic techniques in the framework of classical pseudo-differential calculus. In a nutshell, a parametrix P of a differential operator A is a pseudo-differential operator which can be considered as a generalised inverse, i.e., when applied from the left or right side it yields $PA = I + G_l$, $AP = I + G_r$, where the remainders G_l and G_r are left and right Green operators, respectively. In contrast to the standard calculus of pseudo-differential operators on smooth manifolds, our calculus applies to singular spaces with conical, edge and corner type singularities as well, cf. the monographs [2, 9, 15] for a detailed exposition. In the smooth case, remainders correspond to compact operators with smooth kernel function, whereas in the singular calculus Green operators encode important asymptotic information which we want to extract. Acting on (3) with the parametrix from the left yields

$$\tau_{n+1} = -PV^{(2)} - Pf_{V^{(2)}\tau_n} + Pf_{V^{(1)}\tau_n} - Pf_{V^{(2)}\circ\tau_n} - Pf_{\tau_n\circ V^{(2)}\circ\tau_n} - G_l\tau_{n+1}. \tag{4}$$

The parametrix P maps in a controlled manner between functions with certain asymptotic behaviour which means that we can derive from the asymptotic properties of the terms on the right hand side of (3) its effect on the asymptotic behaviour of τ_{n+1}. Furthermore it is an essential property of G_l that the operator maps onto a space with specific asymptotic type. Therefore the asymptotic type of $G_l\tau_{n+1}$ is fixed and does not depend on τ_{n+1}. Thus we have full control on the asymptotic properties of the right hand side of (4) and consequently on the asymptotic type of the iterated pair-amplitude τ_{n+1}.

Let us briefly outline how one gets the singular asymptotic behaviour of individual Goldstone diagrams within this framework. The iteration scheme discussed in the previous paragraph can be actually further decomposed by taking into account the linearity of the differential operator A. Instead of solving the first iterated equation (2) as a whole, let us consider the decomposition

$$A\tau_{1,1} = -f_{V^{(2)}\tau_0}, \quad A\tau_{1,2} = f_{V^{(1)}\tau_0}, \quad A\tau_{1,3} = -f_{V^{(2)}\circ\tau_0}, \quad A\tau_{1,4} = -f_{\tau_0\circ V^{(2)}\circ\tau_0},$$

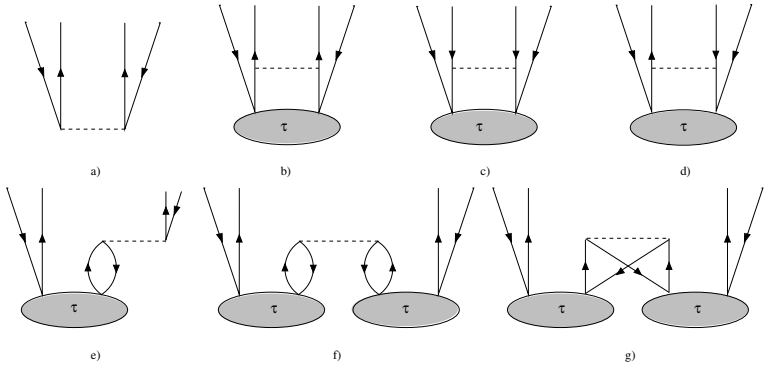


FIGURE 1. Goldstone diagrams taken into account by our CC model.

from which one recovers the first iterated solution via the sum

$$\tau_1 = \tau_0 + \tau_{1,1} + \tau_{1,2} + \tau_{1,3} + \tau_{1,4}, \tag{5}$$

where each term actually corresponds to an individual Goldstone diagram. According to Goldstone's theorem, cf. [11], each of these Goldstone diagrams is represented by a connected graph. In the next iteration step, one can further use the decomposition (5) to construct the interaction terms on the right hand side. For each new term on the right hand side obtained in such a manner one can again solve the corresponding equation which leads to the decomposition of the second iterated solution into Goldstone diagrams

$$\tau_2 = \tau_0 + \tau_{1,1} + \tau_{1,2} + \tau_{1,3} + \tau_{1,4} + \tau_{2,1} + \tau_{2,2} + \cdots$$

This process can be continued through any number of successive iteration steps. Therefore from a diagrammatic point of view, iteration schemes correspond to the summation of an infinite series of Goldstone diagrams which represents a pair-amplitude.

Our main result concerning Goldstone diagrams is summarised in the following theorem where τ_{RPA} can be any Goldstone diagram which appears in the RPA-CC model, depicted in Fig. 1. We want to emphasise that this result refers to the real RPA-CC model without requiring any of the simplifications discussed before.

Theorem 1. *Goldstone diagrams of RPA-CC pair-amplitudes*[1] *can be considered as kernel functions of classical pseudo-differential operators without logarithmic terms in their asymptotic expansion. Classical symbols corresponding to Goldstone diagrams, i.e.,* $\sigma_{\mathrm{RPA}}(\mathbf{x},\boldsymbol{\eta}) := \int e^{-i\mathbf{z}\boldsymbol{\eta}}\tau_{\mathrm{RPA}}(\mathbf{x},\mathbf{z})\,d\mathbf{z}$, *belong to symbol classes* S^p_{cl} *with* $p \leq -4$. *The asymptotic expansion of a Goldstone diagram* τ_{RPA} *with symbol* $\sigma_{\mathrm{RPA}} \in S^p_{\mathrm{cl}}$, *expressed in spherical coordinates* (z,θ,ϕ), *is given by*

$$\tau_{\mathrm{RPA}}(\mathbf{x},\mathbf{z}) \sim \sum_{0\leq j} \tau_{p-j}(\mathbf{x},z,\theta,\phi) \quad \textit{modulo } C^\infty(\mathbb{R}^3\times\mathbb{R}^3), \tag{6}$$

[1]By abuse of notation, we refer to Goldstone diagrams τ_{RPA} either with respect to $(\mathbf{x}_1,\mathbf{x}_2)$ or $(\mathbf{x},\mathbf{z})$ variables, with $\mathbf{x} := \mathbf{x}_1, \mathbf{z} := \mathbf{x}_1 - \mathbf{x}_2$, i.e., $\tau_{\mathrm{RPA}}(\mathbf{x}_1,\mathbf{x}_2) \equiv \tau_{\mathrm{RPA}}(\mathbf{x},\mathbf{z})$.

with

$$\tau_{p-j}(\mathbf{x}, z, \theta, \phi) = z^{j-p-3} \sum_{\substack{l=0 \\ j-p-l \text{ even}}}^{j-p-3} \sum_{m=-l}^{l} g_{j,lm}(\mathbf{x})\, Y_{lm}(\theta, \phi),$$

where functions $g_{j,lm}$ belong to $C^\infty(\mathbb{R}^3)$.

The symbol class of a diagram τ_{RPA} can be determined in the following manner

(i) *Remove all ladder insertions in the diagram.*
(ii) *Count the number of remaining interaction lines n.*

Then the corresponding symbol of the diagram τ_{RPA} belongs to the symbol class S_{cl}^{-4n}.

References

[1] R. J. Bartlett and M. Musial, *Coupled-cluster theory in quantum chemistry*, Rev. Mod. Phys., **79**, (2007), pp. 291–352.

[2] Y. V. Egorov, B.-W. Schulze, *Pseudo-Differential Operators, Singularities, Applications*, Birkhäuser, 1997.

[3] H.-J. Flad, G. Harutyunyan, R. Schneider and B.-W. Schulze, *Explicit Green operators for quantum mechanical Hamiltonians. I. The hydrogen atom*, manuscripta math., **135**, (2011), pp. 497–519.

[4] H.-J. Flad, G. Harutyunyan and B.-W. Schulze, *Singular analysis and coupled cluster theory*, PCCP, **17**, (2015), pp. 31530–31541.

[5] H.-J. Flad, G. Harutyunyan and B.-W. Schulze, *Asymptotic parametrices of elliptic edge operators*, J. Pseudo-Differ. Oper. Appl., **7**, (2016), pp. 321–363.

[6] H.-J. Flad, G. Flad-Harutyunyan and B.-W. Schulze, *Explicit Green operators for quantum mechanical Hamiltonians. II. Edge singularities of the helium atom*, preprint: arXiv:1801.07552 [math-ph].

[7] H.-J. Flad and G. Flad-Harutyunyan, *Singular analysis of RPA diagrams in coupled cluster theory*, submitted to ESAIM: M2AN, preprint: arXiv:1801.07573 [math-ph].

[8] S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof and T. Østergaard Sørensen, *Analytic structure of many-body Coulombic wave functions*, Comm. Math. Phys., **289**, (2009), pp. 291–310.

[9] G. Harutyunyan and B.-W. Schulze, *Elliptic Mixed, Transmission and Singular Crack Problems*, EMS Tracts in Mathematics, Vol. **4**, European Math. Soc., (2008).

[10] A. Laestadius and S. Kvaal, *Analysis of the extended coupled-cluster method in quantum chemistry*, preprint: arXiv:1702.04317v1.

[11] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, Springer, Berlin, (1986).

[12] T. Rohwedder, *The continuous coupled cluster formulation for the electronic Schrödinger equation*, ESAIM: M2AN, **47**, (2013), pp. 421–447.

[13] T. Rohwedder and R. Schneider, *Error estimates for the coupled cluster method*, ESAIM: M2AN, **47**, (2013), pp. 1553–1582.

[14] R. Schneider, *Analysis of the projected coupled cluster method in electronic structure calculation*, Num. Math., **113**, (2009), pp. 433–471.

[15] B.-W. Schulze, *Boundary Value Problems and Singular Pseudo-Differential Operators*, Wiley, (1998).

Dynamical low-rank approximation

Christian Lubich

The talk reviewed differential equations on manifolds of matrices or tensors of low rank. They serve to approximate, in a low-rank format, large time-dependent matrices and tensors that are either given explicitly via their increments or are unknown solutions of high-dimensional differential equations, such as multi-particle time-dependent Schrödinger equations.

Recently developed numerical time integrators are based on splitting the projector onto the tangent space of the low-rank manifold at the current approximation. In contrast to all standard integrators, these projector-splitting methods are robust with respect to the presence of small singular values in the low-rank approximation. This robustness relies on geometric properties of the low-rank manifolds: in each substep of the algorithm, the approximation moves along a flat subspace of the low-rank manifold. In this way, high curvature due to small singular values does no harm.

The talk is based on work done intermittently over the last decade with Othmar Koch, Bart Vandereycken, Ivan Oseledets, Emil Kieri and Hanna Walach.

References

[1] E. Kieri, C. Lubich and H. Walach, *Discretized dynamical low-rank approximation in the presence of small singular values*, SIAM J. Numer. Anal., **54**, (2016), pp. 1020–1038.
[2] O. Koch and C. Lubich, *Dynamical low-rank approximation*, SIAM J. Matrix Anal. Appl., **29**, (2007), pp. 434–454.
[3] O. Koch and C. Lubich, *Dynamical tensor approximation*, SIAM J. Matrix Anal. Appl., **31**, (2010), pp. 2360–2375.
[4] C. Lubich, *Time integration in the multiconfiguration time-dependent Hartree method of molecular quantum dynamics*, Applied Mathematics Research eXpress, (2015), pp. 311–328.
[5] C. Lubich and I. V. Oseledets, *A projector-splitting integrator for dynamical low-rank approximation*, BIT Numer. Math., **54**, (2014), pp. 171–188.
[6] C. Lubich, I. V. Oseledets and B. Vandereycken, *Time integration of tensor trains*, SIAM J. Numer. Anal., **53**, (2015), pp. 917–941.
[7] C. Lubich, B. Vandereycken and H. Walach, *Time integration of rank-constrained Tucker tensors*, SIAM J. Numer. Anal., **56**, (2018), to appear.

Minimal Surface Hopping

Caroline Lasser

This talk aims at the mathematical underpinning of molecular quantum dynamics beyond the Born–Oppenheimer approximation.

Born-Oppenheimer approximation describes the vibrational quantum dynamics of a molecule given the system's electronic eigenvalue surfaces. Let us denote by x and y the nuclear and the electronic coordinates of a molecule, respectively, and by $E_m(x)$, $m \geq 0$, the electronic eigenvalue surfaces, that are the eigenvalues of

the electronic Hamiltonian $H_{\mathrm{el}}(x)$. Assuming that all the nuclei have identical mass $M > 0$, the Born-Oppenheimer equations take the form

$$i\hbar\partial_t\psi_m(x,t) = -\frac{\hbar^2}{2M}\Delta_x\psi_m(x,t) + E_m(x)\psi_m(x,t). \tag{1}$$

These equations yield an adequate description of vibrational quantum dynamics as long as the derivatives of the electronic eigenfunctions $u_m(x)$ with respect to the nuclear coordinates x are not too large. In almost every molecular system, however, there are avoided or true crossings of electronic eigenvalue surfaces. That is, there are nuclear configurations x such that the gap

$$g_{mn}(x) = |E_m(x) - E_n(x)|$$

between different eigenvalue surfaces becomes small or even zero. The derivatives of the electronic eigenfunctions are intimately linked to the eigenvalue differences, since

$$\begin{aligned}&\langle u_m(x,y) \mid \nabla_x u_n(x,y)\rangle_y \\ &\quad = -\frac{\langle u_m(x,y) \mid (\nabla_x H_{\mathrm{el}}(x))u_n(x,y)\rangle_y}{E_m(x) - E_n(x)}\ .\end{aligned}$$

Hence, in the presence of small or even vanishing eigenvalue gaps the single surface equations (1) have to be replaced by coupled evolution equations.

A particularly simple and widely popular way to deal with multiple surface dynamics is surface hopping. It combines the following two constitutive elements:

a) classical equations of motion for nuclear positions along the electronic surfaces,
$$M\,\ddot{x}(t) = -\nabla_x E_m(x(t)),$$
b) hopping between different electronic surface dynamics.

The aim of the talk is to present a minimalist hopping mechanism and its mathematical justification according to [4, 3]. Minimal surface hopping monitors the time-evolution of a simple non-Born-Oppenheimer indicator as for the example the evolution of the surface gap along a classical trajectory,

$$t \mapsto g_{mn}(x(t)).$$

Whenever a local minimum is attained, say at time $t = t_*$, the probability of switching to the other surface dynamics is determined according to the dynamic Landau-Zener rate

$$p_{mn} = \exp\left(-\frac{\pi}{2\hbar}\sqrt{\frac{g_{mn}(x(t))^3}{\frac{d^2}{dt^2}\,g_{mn}(x(t))}\Big|_{t=t_*}}\right),$$

see [1] for an application to the twelve-dimensional dynamics of the ammonia cation.

The mathematical underpinning of minimal surface hopping draws from the theory of microlocal normal forms for Schrödinger systems with avoided and actual eigenvalue crossings, see for example [2]. In a nutshell, microlocal normal form

theorems construct invertible operators $\mathcal{T}_{\rm loc}$ and coupling parameters $\delta_{\rm loc}$ such that

$$\mathcal{T}_{\rm loc}\left(-i\hbar\partial_t - \frac{\hbar^2}{2M}\Delta_x + \begin{pmatrix} E_m(x) & 0 \\ 0 & E_n(x)\end{pmatrix} + \text{coupling operators}\right)\mathcal{T}_{\rm loc}^{-1}$$

$$\approx -i\hbar\partial_t + \begin{pmatrix} t & \delta_{\rm loc} \\ \delta_{\rm loc} & -t\end{pmatrix}$$

The resulting ordinary differential equation

$$i\hbar\,\dot\varphi(t) = \begin{pmatrix} t & \delta_{\rm loc} \\ \delta_{\rm loc} & -t\end{pmatrix}\varphi(t)$$

is then used for a quantitative analysis of the hopping mechanism, while the almost explicit construction of the invertible operator $\mathcal{T}_{\rm loc}$ allows to retransfer the key data back to the Schrödinger system.

References

[1] A. Belyaev, W. Domcke, C. Lasser and G. Trigila, *Nonadiabatic nuclear dynamics of the ammonia cation studied by surface hopping classical trajectory calculations*, J. Chem. Phys., **142**, (2015), 104307.

[2] C. Fermanian-Kammerer and P. Gérard, *Mesures semi-classique et croisements des modes*, Bull. Soc. Math. France, **130**, (2002), pp. 123–168.

[3] C. Fermanian-Kammerer and C. Lasser, *An Egorov Theorem for avoided crossings of eigenvalue surfaces*, Comm. Math. Phys., **353**, (2017), pp. 1011–1057.

[4] C. Lasser and S. Teufel, *Propagation through Conical Crossings: an Asymptotic Semigroup*, Comm. Pure Appl. Math., **58**, (2005), pp. 1188–1230.

The density to potential mapping in quantum dynamics: recent results

Robert van Leeuwen

(joint work with Michael Ruggenthaler, Markus Penz and Søren Nielsen)

We address the question whether the particle density of a quantum many-particle system is uniquely determined by the external one-body potential and which properties this external potential must have to generate a certain density. The question is of particular importance to time-dependent density-functional theory [1]. The setting of the problem is the time-dependent Schrödinger equation (TDSE) for a system of N particles:

$$i\partial_t\Psi(\underline{\mathbf{x}},t) = \hat H(t)\Psi(\underline{\mathbf{x}},t) \qquad \Psi(\underline{\mathbf{x}},t_0) = \Psi_0(\underline{\mathbf{x}})$$

where Ψ is the many-particle wave-function, $\hat H(t)$ is a time-dependent Hamilton operator (dependent on a time variable $t\in\mathbb{R}$) specified below and $\underline{\mathbf{x}} = (\mathbf{x}_1,\dots,\mathbf{x}_N)$ is a collection of N space-spin coordinates in which $\mathbf{x}_i = (\mathbf{r}_i,\sigma_i)$ where $\mathbf{r}_i\in\mathbb{R}^3$ and σ_i a discrete spin variable that assumes the values ±1. The initial state at time t_0 is denoted by Ψ_0. The wave-function is required to be anti-symmetric under permutation of the N variables $\mathbf{x}_i$, i.e. if $\mathcal{P}\underline{\mathbf{x}} = (\mathbf{x}_{\mathcal{P}(1)},\dots,\mathbf{x}_{\mathcal{P}(N)})$ is a permutation $\mathcal{P}$ of the variables $\mathbf{x}_i$ then $\Psi(\mathcal{P}\underline{\mathbf{x}},t) = (-1)^{|\mathcal{P}|}\Psi(\underline{\mathbf{x}},t)$ with $|\mathcal{P}|$ the

number of transpositions out which the permutation is composed. The Hamilton operator is composed out of three terms

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

in which $\hat{T}$ represents the kinetic energy operator, $\hat{V}(t)$ the time-dependent external potential and $\hat{W}$ the inter-particle interactions. The operator $\hat{T}$ is essentially given by the $3N$-dimensional Laplacian operator Δ_{3N}, explicitly we have

$$\hat{T} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} = -\frac{1}{2}\Delta_{3N}$$

where ∇_i is the gradient for variable $\mathbf{r}_i$. The operators $\hat{V}(t)$ and $\hat{W}$ are defined by

$$\hat{V}(t) = \sum_{i=1}^{N} v(\mathbf{r}_i, t) \qquad , \qquad \hat{W} = \sum_{i>j}^{N} w(\mathbf{r}_i - \mathbf{r}_j)$$

and represent sums over one-body and two-body potentials respectively. The external potential $v(\mathbf{r}, t)$ is dependent on time and represents, for example, the attractive Coulomb potential of fixed external nuclear point charges plus an added laser field. The two-body interaction $w(\mathbf{r})$ is typically taken to be a repulsive Coulombic interaction but we do not specify the function spaces for which the TDSE is well-defined here (see [2, 3] for mathematical details). We consider two relevant physical quantities, namely the density $n(\mathbf{r}, t)$ and the current density $\mathbf{j}(\mathbf{r}, t)$ which are defined as

$$n(\mathbf{r}, t) = N \sum_{\sigma=\pm 1} \int d^{N-1}\underline{\mathbf{x}}\, |\Psi(\underline{\mathbf{x}}, t)|^2$$

$$\mathbf{j}(\mathbf{r}, t) = \frac{N}{2i} \int d^{N-1}\underline{\mathbf{x}}\, \left[\Psi^*(\underline{\mathbf{x}}, t)\nabla\Psi(\underline{\mathbf{x}}, t) - (\nabla\Psi^*(\underline{\mathbf{x}}, t))\Psi(\underline{\mathbf{x}}, t)\right]$$

where $d^{N-1}\underline{\mathbf{x}}$ denotes an integration over all variables $\mathbf{r}_i$ $(i = 2, \ldots, N)$ and a sum over the corresponding spin variables σ_i except for one variable, which we denote by $\mathbf{x} = (\mathbf{r}, \sigma)$. The aim is to determine in which way the density is determined by the external potential, provided we fix the operators $\hat{T}$ and $\hat{W}$ as well as the initial state. We notice that changing $v(\mathbf{r}, t)$ by a purely time-dependent function $v(\mathbf{r}, t) \to v(\mathbf{r}, t) + C(t)$ will only change the solution of the TDSE by a phase factor, $\Psi(\mathbf{x}, t) \to \Psi(\mathbf{x}, t) \exp\left(-i \int_{t_0}^{t} d\bar{t} C(\bar{t})\right)$ and leaves the density (as well as any other physical observable) invariant. We therefore consider the equivalence class of potentials (gauge class), which we denote by $[v(\mathbf{r}, t)]$, of potentials that differ by a purely time-dependent function. The central theme of this presentation is the one-to-one correspondence between the density and initial state and the gauge class of external potentials:

$$(n(\mathbf{r}, t), \Psi_0(\underline{\mathbf{x}})) \leftrightarrow [v(\mathbf{r}, t)]$$

In other words, the knowledge of the density and the initial state gives enough information to recover the external potential up to a purely time-dependent function. A physicist's proof of this statement was first presented by Runge and Gross [4] although the one-to-one correspondence was already stated by Peuckert [5]. A rigorous mathematical justification of the Runge-Gross argument was given by Fournais et al. [6] but only for the class of potentials and initial states that are infinitely differentiable in space and time and which, in particular, excludes the Coulomb interaction between the particles. We have therefore in recent works [7, 8, 9, 2] pursued a different proof strategy to extend the domain of allowed potentials and initial states. This strategy is based on the quantum fluid formulation of the quantum many-body problem in the form:

$$\partial_t n(\mathbf{r},t) = -\nabla\cdot\mathbf{j}(\mathbf{r},t) \tag{1}$$

$$\partial_t \mathbf{j}(\mathbf{r},t) = -n(\mathbf{r}t)\nabla v(\mathbf{r},t) - \mathbf{Q}(\mathbf{r},t) \tag{2}$$

in which the three spatial components of the vector $\mathbf{Q}(\mathbf{r},t)$ are given by

$$Q_k(\mathbf{r},t) = \sum_{i=1}^{3} \partial_i T_{ik}(\mathbf{r},t) + W_k(\mathbf{r},t)$$

where ∂_i is a spatial derivative and T_{ik} and W_k are defined as

$$T_{ik}(\mathbf{r},t) = \frac{N}{2}\sum_{\sigma=\pm1}\int d^{N-1}\underline{\mathbf{x}}\left([\partial_i\Psi^*(\underline{\mathbf{x}},t)\partial_k\Psi(\underline{\mathbf{x}},t) + (i\leftrightarrow k)] - \frac{1}{2}\partial_i\partial_k|\Psi(\underline{\mathbf{x}},t)|^2\right)$$

$$W_k(\mathbf{r},t) = N\int d^{N-1}\underline{\mathbf{x}}\,\partial_k w(\mathbf{r}-\mathbf{r}_2)|\Psi(\underline{\mathbf{x}},t)|^2$$

Eqs. (1) and (2) represent a quantum fluid formulation of the many-body problem. Combining these two equations gives an equation that directly relates the density and the external potential:

$$-\nabla(n(\mathbf{r},t)\nabla v(\mathbf{r},t)) = q(\mathbf{r},t) - \partial_t^2 n(\mathbf{r},t) \tag{3}$$

where we defined $q(\mathbf{r},t) = \nabla\cdot\mathbf{Q}(\mathbf{r},t)$. This equation has been used in fixed-point scheme to construct the potential from a given density and to extend the domain of potentials and initial states beyond the ones presented in [6]. The details of this procedure are given in [7, 8, 9, 2] and the procedure was numerically implemented [10, 11, 12]. An important recent theorem in this context was proven by M. Penz in [3] in the framework of non-autonomous evolution equations in Banach spaces which provides an important regularity theorem for the TDSE as a special case. The incorporation of this result in a rigorous treatment of the fixed-point proof based on Eq. (3) is subject of current research.

References

[1] C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications*, Oxford University Press, Oxford, (2012).

[2] M. Penz, *The Density-Potential Mapping in Quantum Dynamics*, PhD Thesis University of Innsbruck, arXiv:1610.05552, (2016).

[3] M. Penz, *Regularity for evolution equations with non-autonomous perturbations in Banach spaces*, arXiv:1801.03361, (2018).
[4] E. Runge and E. K. U. Gross, *Density-Functional Theory for Time-Dependent Systems*, Phys. Rev. Lett., **52**, 997, (1984).
[5] V. Peuckert, *A new approximation method for electron systems*, J. Phys. C.: Solid State Phys. **11**, 4945, (1978).
[6] S. Fournais, J. Lampart, M. Lewin and T. Østergaard-Sørensen, *Coulomb potentials and Taylor expansions in time-dependent density-functional theory*, Phys. Rev. A, **93**, 062510, (2016).
[7] M. Ruggenthaler and R. van Leeuwen, *Global fixed-point proof of time-dependent density-functional theory*, EPL, **95**, 13001, (2011).
[8] M. Ruggenthaler, K. J. H. Giesbertz, M. Penz and R. van Leeuwen, *Density-potential mappings in quantum dynamics*, Phys. Rev. A, **85**, 052504, (2012).
[9] M. Ruggenthaler, M. Penz and R. van Leeuwen, *Existence, uniqueness, and construction of the density-potential mapping in time-dependent density-functional theory*, Topical Review, J. Phys. Condens. Matter, **27**, 203202, (2015).
[10] S. E. B. Nielsen, M. Ruggenthaler and R. van Leeuwen, *Many-body quantum dynamics from the density*, EPL, **101**, 33001, (2013).
[11] S. E. B. Nielsen, M. Ruggenthaler and R. van Leeuwen, *Quantum Control of Many-Body Systems by the Density*, arXiv:1412.3794, (2014).
[12] S. E. B. Nielsen, M. Ruggenthaler and R. van Leeuwen, *Numerical construction of the Runge-Gross mapping*, Eur. Phys. J. B, to be published, (2018).

Recent advances on the domain decomposition strategy for implicit solvation models

Benjamin Stamm

Continuum Solvation models (CSMs) [1, 2, 3, 4, 5] are nowadays part of the standard toolbox of computational chemists. Historically, in the quantum chemistry community, polarizable CSMs such as the Polarizable Continuum Model (PCM) [1] or the Conductor-like Screening Model (COSMO) [6] have been developed as a cheap, but physically sound way, to include solvation effects in the quantum mechanical (QM) description of a molecule and its properties. As the computational cost is usually dominated by the solution of the QM equations, the computational performance of CSM have not been historically taken into much consideration, as the setup and solution of the CSM equations, which are equivalent in some way to solving Poisson's equation in a heterogeneous dielectric medium (see below), has always been assumed to be a negligible additional computational cost. Due to advances in hardware, more efficient implementations and the spread of linear scaling techniques within quantum chemistry, such an assumption started to be less and less true in the last decade. Further, the diffusion of multiscale methods such as quantum mechanics/molecular mechanics (QM/MM) has made large to very large systems accessible to computational chemists. For such systems, the computational cost associated with continuum solvation, which scales as the second or even third power of the size of the system, can easily become the real bottleneck of the calculation [9].

From a modeling viewpoint, there are two main-ingredients for an implicit solvation model. First, the shape of the solute's cavity Ω, or equivalently its surface $\partial\Omega$, is introduced and determines the region where the implicit solvent is present, see Figure 1 (left). The second ingredient is the macroscopic description of the solvent that is used to model the (electrostatic) interaction between the solute and the continuum solvent region. More precisely, the electrostatic potential V generated by the solute's charge ρ is then the solution of

$$-\mathrm{div}(\varepsilon\nabla V) + \kappa^2 V = 4\pi\rho, \qquad \text{in } \mathbb{R}^3, \tag{1}$$

and the electrostatic interaction energy is given by

$$E^s = \frac{1}{2}\int_{\mathbb{R}^3} \rho\, V.$$

Here, the dielectric and Debye-Hückel constants of the solvent are given by ε_{s} and κ_{s} so that

$$\varepsilon = \begin{cases} 0 & \text{in } \Omega, \\ \varepsilon_{\mathsf{s}} & \text{in } \Omega^{\mathsf{c}}, \end{cases} \qquad \kappa = \begin{cases} 0 & \text{in } \Omega, \\ \kappa_{\mathsf{s}} & \text{in } \Omega^{\mathsf{c}}. \end{cases} \tag{2}$$

In this talk, we gave a review of the latest developments of the family of domain decomposition (dd) methods for polarizable continuum models. We started with the derivation of the domain decomposition method for COSMO [7, 8, 9, 10], i.e. with $\varepsilon_{\mathsf{s}} = \infty$ and $\kappa_{\mathsf{s}} = 0$ in (1). Indeed, in this particular case, the problem is reduced to the bounded domain Ω (the solute's cavity) which is then split into the union of overlapping and possibly scaled Van der Waals balls Ω_i and equation (1) is solved inside each ball and coupled through appropriate boundary conditions. Numerical illustrations were underlying the efficiency of the present method compared to the state-of-the-art.

This model can then be generalized to the PCM [11, 12] which corresponds to equation (1) with $\kappa_{\mathsf{s}} = 0$ (no ionic screening) still using the Van der Waals cavity but for finite ε_{s}. The corresponding domain decomposition approach, but this time for an equivalent integral equation formulation as the problem is posed on the entire unbounded free space $\mathbb{R}^3$, was introduced.

Recent results on larger molecules indicate the the model for the cavity consisting of the union of balls in form of the (possibly scaled) Van der Waals cavity does not provide phenomenologically accurate results. In turn, the Solvent Excluded Surface (SES) seems to be a favorable alternative. We highlighte the mathematical structure and recent analysis of the SES [14, 15], see also Figure 1 (right) for the SES of caffeine, and continued with a new domain decomposition approach for the PCM that uses the cavity the SES-cavity [13]. We discussed in detail the derivation of the numerical method and presented some numerical tests. Finally, the extension [16] to the full linearized Poisson-Boltzmann equation (1) was briefly discussed.

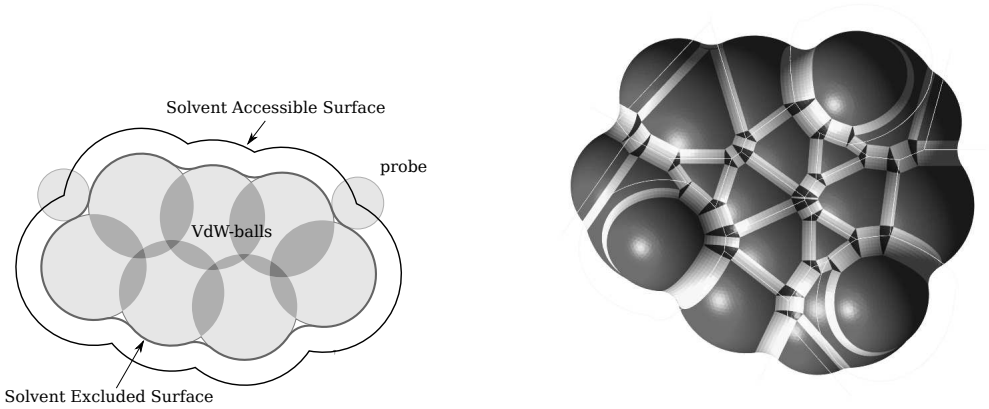


FIGURE 1. An illustration of the different molecular surfaces (left) and the Solvent Excluded Surface (SES) for caffeine (right).

REFERENCES

[1] J. TOMASI, B. MENNUCCI AND R. CAMMI, *Quantum Mechanical Continuum Solvation Models*, Chem. Rev., **105** (8), (2005), pp. 2999–3093.

[2] B. MENNUCCI, *Continuum Solvation Models: What Else Can We Learn from Them?*, J. Phys. Chem. Lett., **1** (10), (2010), pp. 1666–1674.

[3] CH. CRAMER AND D.G. TRUHLAR, *Implicit Solvation Models: Equilibria, Structure, Spectra and Dynamics*, Chem. Rev., **99** (8), (1999), pp. 2161–2200.

[4] B. MENNUCCI, *Polarizable continuum model*, WIREs Comput. Mol. Sci., **2** (3), (2012), pp. 386–404.

[5] F. LIPPARINI AND B. MENNUCCI, *Perspective: Polarizable continuum models for quantum-mechanical descriptions*, J. Chem. Phys., **16** (144), (2016), 160901.

[6] A. KLAMT AND G. SCHÜÜRMANN, *COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient*, J. Chem. Soc., Perkin Trans. 2, **5**, (1993), pp. 799–805.

[7] E. CANCÈS, Y. MADAY AND B. STAMM, *Domain decomposition for implicit solvation models*, J. Chem. Phys., **139** (5), (2013), 054111.

[8] F. LIPPARINI, B. STAMM, E. CANCÈS, Y. MADAY AND B. MENNUCCI, *Fast domain decomposition algorithm for continuum solvation models: Energy and first derivatives*, J. Chem. Theory Comput., **9** (8), (2013), pp. 3637–3648.

[9] F. LIPPARINI, L. LAGARDÈRE, G. SCALMANI, B. STAMM, E. CANCÈS, Y. MADAY, J.-P. PIQUEMAL, M. J. FRISCH AND B. MENNUCCI, *Quantum calculations in solution for large to very large molecules: A new linear scaling QM/continuum approach*, J. Phys. Chem. Lett., **5** (6), (2014), pp. 953–958.

[10] F. LIPPARINI, G. SCALMANI, L. LAGARDÈRE, B. STAMM, E. CANCÈS, Y. MADAY, J.-P. PIQUEMAL, M. J. FRISCH AND B. MENNUCCI, *Quantum, classical, and hybrid QM/MM calculations in solution: General implementation of the ddCOSMO linear scaling strategy*, J. Chem. Phys., **18** (141), (2014), 184108.

[11] B. STAMM, E. CANCÈS, F. LIPPARINI AND Y. MADAY, *A new discretization for the polarizable continuum model within the domain decomposition paradigm*, J. Chem. Phys., **5** (144), (2016), 054101.

[12] P. GATTO, F. LIPPARINI AND B. STAMM, *Computation of Forces arising from the Polarizable Continuum Model within the Domain-Decomposition Paradigm*, J. Chem. Phys., **22** (147), (2017), 224108.

[13] Ch. Quan, B. Stamm, and Y. Maday, *Polarizable Continuum Model based on the Solvent Excluded Surface*, Math. Models Meth. Appl. Sci, (2018), in press (available as e-print), doi.org/10.1142/S0218202518500331.
[14] Ch. Quan and B. Stamm *Mathematical analysis and calculation of molecular surfaces*, J. Comput. Phys., **322**, (2017), pp. 760–782.
[15] Ch. Quan and B. Stamm, *Meshing molecular surfaces based on analytical implicit representation*, J. Mol. Graph. Model., **71**, (2016), pp. 200–210.
[16] Ch. Quan, B. Stamm and Y. Maday *A Domain Decomposition Method for the Poisson-Boltzmann Solvation Models*, Hal-preprint https://hal.archives-ouvertes.fr/hal-01489262, (2018).

How to obtain the interacting Green's functions of many-body quantum systems from a differential equation?

Lucia Reining

(joint work with Arjan Berger, Pierluigi Cudazzo, Stefano Di Sabatino, Matteo Guzzo, Giovanna Lani, Bernardo Mendoza, Pina Romaniello, Adrian Stan, Walter Tarantino, Marilena Tzavala and Jianqiang Sky Zhou)

Many-body perturbation theory is a powerful approach to describe many properties of materials. Here we are interested in the one-body Green's function of interacting electron systems, but much of the discussion can be generalized.

To treat electrons in the presence of the Coulomb interaction, most often one solves a Dyson equation, namely an integral equation of the type

$$G(1,2) = G_0(1,2) + G_0(1,\bar{3})\Sigma(\bar{3},\bar{4})G(\bar{4},2). \tag{1}$$

Here G is the Green's function of the interacting system, and G_0 is the Green's function in absence of interaction. The self-energy kernel Σ contains all interaction effects, and it is in general unknown and has to be approximated. Arguments (i) stand for a space, spin and time argument: $(i) \equiv (\mathbf{r}_i, \sigma_i, t_i)$, and overlined arguments are integrated over: $A(1,\bar{3})B(\bar{3},2) \equiv \int d3A(1,3)B(3,2)$.

The state-of-the art approximation for Σ is Hedin's GW approximation [1], where the self-energy is the product of the interacting Greens function and the Coulomb interaction, dressed by the linear response of all electrons to the propagation of a particle. Besides density functional theory, this is one of the most widely used approaches for electronic structure calculations in a broad range of materials. However, sometimes the GW approximation and related approaches are not sufficient, in particular when one is interested in structures that appear in excitation spectra exclusively because of the interaction (these structures are called satellites). It also breaks down in the case of strong coupling, where the quasi-particle picture is no longer adequate (i.e. when one cannot at all identify structures in an interacting spectrum with slightly modified peaks in the non-interacting spectrum).

We explore an alternative route to the calculation of interacting electron Green's functions. It is based on a set of functional differential equations
(2)

$$G^u(1,2) = G_0(1,2) + G_0(1,\bar{3})\left\{[u(\bar{3}) + v_{Hu}(\bar{3})]G^u(\bar{3},2) + iv_c(\bar{3},\bar{4})\frac{\delta G^u(\bar{3},2)}{\delta u(\bar{4}^+)}\right\}.$$

This set of equations [2] is created by applying a fictitious perturbing potential u to the system, which is then set to zero at the end of the derivation, such that $\lim_{u\to 0} G^u = G$. Here v_{Hu} is the Hartree potential, i.e. the mean field potential due to the classical charge distribution of all electrons. All effects due to exchange and correlation are contained in the derivative.

This set of equations can be used to generate the perturbation series. Here, instead, we are interested in solving the differential equations directly, in order to obtain non-perturbative expressions. Results along several lines have already been obtained, in particular, we have derived approximations close to the cumulant expansion for the one-body Green's function [3, 4, 5], and, by projecting the equations onto a simple model that yields a scalar differential equation, we have discussed fundamental questions such as problems of multiple solutions in many-body perturbation theory [6, 7, 8, 9].

However, many important questions remain still open. The main issues brought to the audience of the workshop are the following:

- What could be a general strategy (analytical and/or numerical) to solve the set of equations and to select the physical solution?
- What is the meaning of the various solutions? Is there a link to phase transitions?
- Could one derive a modified set of differential equations with only one, or at least less, solutions?
- What is the impact of our findings on many-body perturbation theory (there seem to be problems in a regime of strong interaction)?
- How could we restrict the domain of "physical" Green's functions such that we can parametrize the solution, and derive a set of equations for these parameters? This would eliminate spurious solutions.

The discussion concerning these questions has been prepared both using the simple model and the full equations.

References

[1] L. Hedin, *New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*, Phys. Rev., **139**, A796, (1965).

[2] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics*, W. A. Benjamin, New York, (1962).

[3] M. Guzzo et al., *Valence Electron Photoemission Spectrum of Semiconductors: Ab Initio Description of Multiple Satellites*, Phys. Rev. Lett., **107**, p. 166401, (2011).

[4] M. Guzzo et al., *Multiple satellites in materials with complex plasmon spectra: From graphite to graphene*, Phys. Rev. B, **89**, pp. 085425, (2014).

[5] J. Zhou et al. *Dynamical effects in electron spectroscopy*, J. Chem. Phys., **143**, p. 184109, (2015).

[6] G. Lani, P. Romaniello, and L. Reining, *Approximations for many-body Green's functions: insights from the fundamental equations*, New J. Phys., **14**, p. 013056, (2012).
[7] J. A. Berger et al., *Solution to the many-body problem in one point*, New J. Phys., **16**, p. 113025, (2014).
[8] A. Stan et al., *Unphysical and physical solutions in many-body theories: from weak to strong correlation*, New J. Phys., **17**, p. 093045, (2015).
[9] W. Tarantino et al., *Self-consistent Dyson equation and self-energy functionals: An analysis and illustration on the example of the Hubbard atom*, Phys. Rev. B, **96**, p. 045124, (2017).

Ab Initio Dynamical Mean Field Theory

Reinhold Schneider
(joint work with Michael Lindsey and Lin Lin)

Finite dimensional model: Full CI and discrete Fock spaces

As an underlying model we consider the electronic Schrödinger equation in full CI spaces or discrete Fock spaces. Given a single particle space of dimension d

$$\mathcal{V}_d = \mathrm{span}\{(\mathbf{r}, s) \mapsto \varphi_i(\mathbf{r}, s) \in \mathbb{C} : i = 1, \dots, d\}$$

which is spanned by orthonormal spin orbitals and is a finite dimensional subspace of the Sobolev space $\mathcal{V}_d \subset \mathcal{V} = H^1(\mathbb{R}^3, \pm\frac{1}{2}) \subset L_2(\mathbb{R}^3, \pm\frac{1}{2})$, the corresponding N-particle full CI space is spanned by Slater determinants. It is the d-fold anti-symmetric tensor product of $\mathcal{V}_d$, denoted by

$$\mathcal{V}_{FCI}^N := \bigwedge_{i=1}^{N} \mathcal{V}_d \ .$$

In the sequel, we will consider the full CI spaces with $N-1$, N and $N+1$ particles. To unify the notation, we may embed these full CI spaces in the discrete Fock space

$$\mathcal{H}_d := \oplus_{N=0}^{d} \mathcal{V}_{FCI}^N \ .$$

The many body Schrödinger Hamiltonian in the discrete Fock-space, or in the corresponding full CI spaces is taken as the the underlying model, for further approximation or model reduction. In second quantization notation the electronic Schrödinger operator is a two particle Hamiltonian given by

$$H = h + H_{II} = \sum_{p,q=1}^{d} f_p^q a_p^\dagger a_p + \sum_{p,q,r,s=1}^{d} u_{r,s}^{p,q} a_r^\dagger a_s^\dagger a_p a_q \tag{1}$$

with the well known single and two electron integrals f_q^p and $u_{r,s}^{p,q}$. Presently, we focus our interest on the following eigenvalue problems:

$$H\Psi_0 = E_0\Psi_0 \ , \ E_0 = E_0^N \in \mathbb{R} \ , \ \Psi_0 \in \mathcal{V}_N^{FCI} \ ,$$
$$H\Psi_p^{N\pm1} = E_p^{N\pm1}\Psi_p^{N\pm1} \ , \ \Psi_n^{N\pm1} \in \mathcal{V}_{N\pm1}^{FCI} \ .$$

All operators $H(z)$, with $z \in \mathbb{R}$, under consideration are supposed to be hermitian!

Single Particle Greens Function

The frequency depending Green's functions $z \mapsto G(z) = (g_{i,j}(z))$, as a function of a complex parameter $z \in \mathbb{C}$ is defined by

$$g_{i,j}(z) := \langle \Psi_0^N, a_i^\dagger (zI + E_0 I + H)^{-1} a_j \Psi_0^N \rangle + \langle \Psi_0^N, a_i (zI + E_0 I - H)^{-1} a_j^\dagger \Psi_0^N \rangle \ ,$$

for almost all $z \in \mathbb{C}$. We are interested in the poles $z = E_0 - E_p^{N-1}$ of $G(z)$.

The self-energy for the Hamiltonian $H = h + H_{II} = \mathbf{a}^\dagger \mathbf{h}(z) \mathbf{a} + H_{II}$, can be defined by

$$-\Sigma(z) := G^{-1}(z) - G_0^{-1}(z) = G^{-1}(z) - ((z + E_0)I - h) \ . \tag{2}$$

Hence the poles of the Green's function are the solutions of the following quasi-particle equations

$$((z + E_0)I - (h + \Sigma(z)))x_p = 0$$

These equations constitute non-linear eigenvalue problems,where the eigenvalue parameter $z = E_N - E_0$ appears in a nonlinear form $zI - \Sigma(z)$. Let us observe that the quasi-particle equations are low dimensional *surrogates* of the original linear eigenvalue problems, that were posed in extremely high-dimensional Full CI spaces. If we are interested in these solutions it seems to be advisable to approximate $\Sigma(z)$ rather than $G(z)$.

Schur Complement

The concept of *Schur complement* is of fundamental importance for the understanding of *dynamical mean field theory*. It shed already light into the nature of the exciton equations.

$$\mathbb{C}^d := \mathbb{C}^n \oplus \mathbb{C}^m = \mathcal{V}_A \oplus \mathcal{V}_B \ , \ \mathbf{G} := \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix}^{-1} = \begin{pmatrix} \mathbf{S}^{-1} & * \\ * & * \end{pmatrix}$$

where the Schur complement $\mathbf{S}$ is given by

$$\mathbf{S} = \mathbf{A} - \Delta = \mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C} \ \ , \ \ \Delta = \mathbf{B}\mathbf{D}^{-1}\mathbf{C} \ \in \mathbb{C}^{n \times n} \ .$$

It is obvious that, if $\mathbf{D}^{-1}(z)$ exists:

$$\mathbf{G}^{-1}(z) \in \mathbb{C}^{d \times d} \text{ is invertible } \Leftrightarrow \mathbf{S}(z) \in \mathbb{C}^{n \times n} \text{ is invertible.}$$

Which suggests that the Schur complement $\mathbf{S}(z) \in \mathbb{C}^{n \times n}$ on the subspace $\mathbb{C}^n$ provides a good surrogate for $\mathbf{G}^{-1}(z)$.

Fragmentation

We decompose the system into K fragments $A_k : k = 1, \ldots K$, by a decomposition of the basis set. We have in mind that this corresponds to a spatial decomposition if the orthonormal orbital basis functions φ_i are localized. We define the local single particle spaces and the decomposition of the single particle space:

$$\mathcal{V}_d = \oplus_{k=1}^K \mathcal{V}_{A_k} = \mathcal{V}_A \oplus \mathcal{V}_{A^c} \ , \text{ where } \mathcal{V}_{A_k} := \text{span}\{\varphi_i : i \in A_k\} \ .$$

Given a matrix $\mathbf{G}(z) = (g_{a,b}(z))_{a,b=1,\dots,d}$ with

$$\mathbf{G}(z) = (z\mathbf{I} - (\mathbf{h} + \Sigma(z)))^{-1} \text{ for almost all } z \in \mathbb{C} ,$$

we denote its restriction to a fragment subspace by

$$\mathbf{G}_A(z) := P_A \mathbf{G}(z) P_A := (g_{i,j}(z))_{i,j\in A} ,$$

and hybridization

$$\Delta_A(z) := \mathbf{G}_A^{-1}(z) - P_A \mathbf{G}^{-1}(z) P_A$$

For a given self energy $z \mapsto \Sigma(z)$ and single particle operator h_A, the corresponding $z \mapsto \Sigma_A(z), \Delta_A(z)$ are well defined. The Schur complement is given by

$$G_A^{-1}(z) = ((z + E_0)\delta_{i,j} - (h_{i,j} + \Sigma_{i,j}(z) + \Delta_{i,j}(z)))_{i,j\in A}$$

Since $P_A G(z) P_A = S_A^{-1}(z)$ on fragment A, the Schur complement $S_A(z)$ forms an ideal *surrogate* for the whole system $zI - (h(z) + \Sigma(z))$ on $\mathcal{V}_d$ and also for H on $\mathcal{F}_d$

Basic Assumption. The locality of the self-energy Σ is the basic assumption for the DMFT approximation.

$$(\Sigma_{i,j})_{i,j\in A} =: \Sigma_A, \ \Sigma_{i,j}(z) = 0$$

if $i \in A$, $j \in A^c$. i.e. Σ is block-diagonal.

Impurity problem

For each fragment $A \in \mathcal{B}$, $n = n_A$, the Schur complement covers the influence of the environment. We want to mimic this influence by a quantum mechanical model system. To this end, we consider an impurity system $A \cup B$ with virtual bath $B = B_A$, $\dim \mathcal{V}_B = m = m_A$, on the single particle level $\mathcal{V}_d = \mathcal{V}_A \oplus \mathcal{V}_B$ this reads as

$$zI_{n+m} - h - \Sigma^{imp}(z) = \begin{pmatrix} zI_n - h_A - \Sigma_A(z) & -T^\dagger \\ -T & zI_m - d \end{pmatrix}$$

The corresponding Schur complement

$$s_{i,j}(z) = z\delta_{i,j} - (h_{i,j} + \Sigma_{i,j}(z) + \Delta_{i,j}(z)) \ , \ i,j \in A \ ,$$

has a hybridization term

$$\Delta_{i,j}(z) = \sum_{\nu=d+1}^{d+m} \frac{t_{i,\nu}\overline{t_{\nu,j}}}{c_\nu - z} = \sum_\mu \frac{(X_\mu)_{i,j}}{c_\mu - z}$$

where the matrices $X_\mu \preceq 0$ are positively semi-definite and its rank μ is the multiplicity of c_μ. This corresponds to a quantum mechanical system in the Fock-space $\mathcal{F}_{imp} = \mathcal{F}_A \otimes \mathcal{F}_B \simeq \mathbb{C}^{2^{n+m}}$ where

$$H = H_A \otimes I + \mathbf{a}^\dagger \begin{pmatrix} h_A & t^* \\ t & d \end{pmatrix} \mathbf{a} : \mathcal{F}_{imp} \to \mathcal{F}_{imp}$$

and $H_A = H_{II}|_A$ is the many particle operator at fragment A. The following theorem shows that the self-energy on the bath components vanishes.

Lemma (M. Lindsey & L. Lin)**.** *Locality of self-energy*

$$\Rightarrow \ \Sigma_{imp} := \begin{pmatrix} \Sigma_A^{imp}(z) & 0 \\ 0 & 0 \end{pmatrix}$$

Given the impurity problem, the Green's function $z \mapsto G_A^{imp}(z)$ and self-energy term $z \mapsto \Sigma_A^{imp}(z)$ can be computed for each fragment $A = A_k$, $k = 1, \ldots, K$. Since we want that these quantities reflect the physics of the global system, we assume that $G_A^{imp}(z) = G_A(z)$, or equivalently $\Sigma_A + \Delta_A = \Sigma_A^{imp} + \Delta_A^{imp}$ to holds on each fragment. In a self-consistent iteration cycle, one assumes $\Sigma_A = \Sigma_A^{imp}$, $\Delta_A = \Delta_A^{imp}$. It is not obvious that the self-consistency can be achieved, because of the particular structure of the hybridization. The following definitions and results of M. Lindsey provide an positive answer.

Definition. Let $M \in \mathbb{N}$, $z \mapsto f(z) \in \mathbb{C}^{M\times M}$ is in **PRPRP iff**

$$\exists K \in \mathbb{N}, \text{s.t. } f(z) = \sum_{k=1}^{K} X_k \frac{1}{c_k - z} \ , c_k \in \mathbb{R} \text{ and } \ 0 \preceq X_k \in \mathbb{C}^{M\times M} \ ,$$

Theorem 1 (M. Lindsey)**.** *There exist rational functions $z \mapsto h(z)$ which cannot be represented or approximated by functions the class* **PRPRP***. I.e. the class* **PRPRP** *is not universal.*

Theorem 2. *The Greens functions $z \mapsto G(z)$,*

$$z \mapsto G(z) \in \mathbf{PRPRP} \ , \ z \mapsto G_A(z) \in \mathbf{PRPRP}$$

Theorem 3. *For the self-energy functions $z \mapsto \Sigma(z)$, and $z \mapsto \Sigma_A(z)$ there exists (a static) $\hat{h} \in \mathbb{C}^{M\times M}$ s.t.*

$$z \mapsto \Sigma(z) + \hat{h} \in \mathbf{PRPRP}$$

Theorem 4. *The hybridization functions $z \mapsto \Delta_A(z)$*

$$z \mapsto \Delta_A(z) \in \mathbf{PRPRP}$$

i.e. all are rational functions.

Since $z \mapsto g(z), g_A(z), \Sigma(z), \Sigma_A(z), \Delta_A(z)$, are rational functions, they are analytic outside the poles. Moreover, they are defined by finitely many values $z^i \notin \mathbb{R}$, $i = 1, \ldots, \tilde{P}$. Choosing a sampling set

$$\mathcal{Z} := \{z^i \notin \mathbb{R} \ , \ i = 1, \ldots, P\} \ ,$$

(a popular choice is that $z^i = iy^i$, $y^i \in \mathbb{R}$, are on the imaginary axis) one can compute $\Sigma_{A_k}(z^i), \Delta_{A_k}(z^i)$ for all fragments $A = A_k \in \mathcal{B}$ in a self consistent cycle

$$\Sigma, \Sigma_A \Rightarrow \Delta_A = \Delta_A^{imp} \Rightarrow H_A^{imp} \Rightarrow \Sigma_A^{imp} = \Sigma_A \Rightarrow \Sigma$$

To compute the parameters $t_{i,k}$ for the impurity problem, on each fragment, we propose a new optimization formulation

$$(X_{i,j}, c_\nu) = \ \text{argmin} \ \{\sum_{i=1}^{P} \|\delta_{\ell,j} - \sum_{\nu=1}^{K} \frac{X_\nu}{c_\nu - z^i}\|^2 \ + \ \alpha \sum_{\nu=1}^{K} \|X_\nu\|_* : \ 0 \preceq X_\nu\}$$

where $\|X\|_*$ is the nuclear norm, and $X_{i,j} = \sum_k t_{i,k}\overline{t_{j,k}}$. For given poles $c_\nu \in \mathbb{R}$, this is a convex optimization problem.

Unique continuation principle and Hohenberg-Kohn theorem

Aihui Zhou

The Hohenberg-Kohn theorem addresses that the external potential of a many-body electronic system is a unique functional of the electronic density, apart from a trivial additive constant [3]. Since "all properties of the system are completely determined given only the ground state density" [11], the Hohenberg-Kohn theorem is the theoretical basis of density functional theory (DFT). We note that the mathematical version of the Hohenberg-Kohn theorem is presented in [10].

We understand that DFT has significantly impacted on modern science and engineering (see, e.g., [3, 11, 12, 13, 15, 21]). However, we observe from the literature (c.f., e.g., [5, 6, 7, 10, 14, 17, 18, 19] and references cited therein) that DFT is not entirely elaborated yet. For instance, the existing proofs of Hohenberg-Kohn theorem usually assume directly or indirectly that the particle wavefunction does not vanish on a set of positive measure. We see that the particle wavefunction does not vanish on a set of positive measure is unclear in a real system (c.f. [14, 19]). We refer to [1, 2, 3, 5, 7, 8, 9, 10, 14, 17, 18] and references cited therein for discussions on the Hohenberg-Kohn theorem. In particular, we mention that a modified version of the Hohenberg-Kohn theorem that the external potential of electronic system is a unique functional of the electronic density for Coulomb potentials is presented in [18], in which a direct proof using the Fundamental Theorem of Algebra is provided. We see that no any constant is involved in the modified version [18].

In this talk, we present and prove the Hohenberg-Kohn theorem that if the two potentials differ by more than just a constant on an open set, then the associated densities must be different when the associated wavefunctions do not vanish on an open set [20], which is based a unique continuation principle (see, e.g., [16]).

References

[1] P. W. Ayers, S. Golden, and M. Levy, *Generalizations of the Hohenberg-Kohn theorem: I. Legendre transform constructions of variational principles for density matrices and electron distribution functions*, J. Chem. Phys., **124** (2006), pp. 054101–054107.

[2] N. Hadjisavvas and A. Theophilou, *Rigorous formulation of the Kohn-Sham theory*, Phy. Rev. A., **30** (1984), pp. 2183–2186.

[3] P. Hohenberg and W. Kohn, *Inhomogeneous gas*, Phys. Rev., **136** (1964), pp. B864–B871.

[4] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. A, **140** (1965), pp. 4743–4754.

[5] E. S. Kryachko, *On the original proof by reductio ad absurdum of the Hohenberg-Kohn theorem for many-electron Coulomb systems*, Int. J. Quantum Chem., **103** (2005), pp. 818–823.

[6] E. S. Kryachko, *On the proof by reductio ad absurdum of the Hohenberg-Kohn theorem for ensembles of fractionally occupied states of Coulomb systems*, Int. J. Quantum Chem., **106** (2006), pp. 1795–1798.

[7] E. S. Kryachko and E. V. Ludeña, *Density functional theory: Foundations reviewed*, Phys. Rep., **544** (2014), pp. 123–239.
[8] M. Levy, *University variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solutions of the v-representability problems*, Proc. Nat. Acad. Sci. USA, **76** (1979), pp. 6062–6065.
[9] M. Levy, *Electron densities in search of Hamiltonians*, Phys. Rev. A, **26** (1982), pp. 1200–1208.
[10] E. H. Lieb, *Density functionals for Coulomb systems*, Int. J. Quantum Chem., **24** (1983), pp. 243–277.
[11] R. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press, London, 2004.
[12] R. van Noorden, B. Maher and R. Nuzzo, *The top 100 papers*, Nature, **514** (2014), pp. 550–553.
[13] R. G. Parr and W. T. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
[14] R. Pino, O. Bokanowski, E. V. Ludeña and R. L. Boada, *A re-statement of the Hohenberg-Kohn theorem and its extension to finite subspaces*, Theor. Chem. Account, **118** (2007), pp. 557–561.
[15] S. Redner, *Citation statistics from 110 years of physical review*, Physics Today, June 2005, pp. 49–54.
[16] M. Schechter and B.Simon, *Unique continuation for Schrodinger operators with unbounded potentials*, J. Math. Anal. Appl., **77** (1980), pp. 482–492.
[17] W. Szczepanik, M. Dulak and T. A. Wesolowski, *Comment on "On the original proof by reductio ad absurdum of the Hohenberg-Kohn theorem for many-electron Coulomb systems"*, Int. J. Quantum Chem., **107** (2007), pp. 762–763.
[18] A. Zhou, *Hohenberg-Kohn theorem for Coulomb type systems and its generalization*, J. Math. Chem., **50** (2012), pp. 2746–2754.
[19] A. Zhou, *Some open mathematical problems in electronic structure models and calculations (in Chinese)*, Sci. Sin. Math., **45** (2015), pp. 929–938.
[20] A. Zhou, *A mathematical aspect of Hohenberg-Kohn theorem*, arXiv:1709.07118.
[21] http://www.nature.com/nmat/journal/v15/n4/pdf/nmat4619.pdf.

The localization dichotomy for gapped periodic Schrödinger operators: ordinary vs Chern insulators

Gianluca Panati

(joint work with Domenico Monaco, Adriano Pisante and Stefan Teufel)

The understanding of transport properties of quantum systems out of equilibrium is a crucial challenge in statistical mechanics. A long term goal is to explain the conductivity properties of solids starting from first principles, as *e. g.* from the Schrödinger equation governing the dynamics of electrons and ionic cores. While the general goal appears to be beyond the horizon, some results can be obtained for specific models, in particular for independent electrons in a periodic or random background.

As a general paradigm, in this case the electronic transport properties are related to the spectral type of the Hamiltonian and to the (de-) localization of the corresponding (generalized) eigenstates. However, when ***periodic systems*** are

considered, the Hamiltonian operator has generically purely absolutely continuous spectrum[2]. Therefore, one needs a finer notion of localization, which allows for example to predict when a crystal, in the absence of any external magnetic field, exhibits a zero transverse conductivity, as it happens for ordinary insulators, and when a non-vanishing one, as in the case of the recently realized ***Chern insulators*** [1, 3] predicted by Haldane [5, 6].

Our main message is that such a finer notion of localization is provided by the rate of decay of ***composite Wannier functions*** (CWF) associated to the gapped periodic Hamiltonian operator. Equipped with this notion of localization, we are able to identify two different regimes:

(i) whenever the system is time-reversal (TR) symmetric, there exist exponentially localized composite Wannier functions which are associated to the Bloch bands below the Fermi energy, assuming that the latter is in a spectral gap; correspondingly, the Hall conductivity vanishes;
(ii) viceversa, as soon as the Hall conductivity is non-zero, as it happens for Chern insulators, the composite Wannier functions are delocalized.

The relevant information to discriminate between the two regimes is of topological nature. It is provided by the the triviality of the ***Bloch bundle*** associated to the occupied states, that is, the vector bundle over the Brillouin torus whose fiber over k is spanned by the occupied Bloch states at fixed crystal momentum k.

In a recent paper [9], we rigorously prove a ***Localization-Topology Correspondence***. We consider a gapped periodic (magnetic) Schrödinger operator, and we assume that the Fermi projector corresponds to a *non-trivial* (magnetic) Bloch bundle, as it may happen when TR-symmetry is broken. For example, one might think of the operators modeling Chern insulators or Quantum Hall systems. The rate of decay of composite Wannier functions changes drastically in this case, from exponential to polynomial. We prove that the ***optimal decay*** for a system $w = (w_1, \dots, w_m)$ of CWFs in a non-trivial topological phase is characterized by the divergence of the second moment of the position operator, defined as

$$\langle X^2 \rangle_w \equiv \sum_{a=1}^{m} \int_{\mathbb{R}^d} |x|^2 |w_a(x)|^2 \mathrm{d}x.$$

Heuristically, this corresponds to a power-law decay $|w_a(x)| \asymp |x|^{-\alpha}$, with $\alpha = 2$ for $d = 2$ and $\alpha = 5/2$ for $d = 3$. The former exponent was foreseen by Thouless [14], who also argued that the exponential decay of the Wannier functions is intimately related to the vanishing of the Hall current.

More precisely, we prove—under suitable technical hypothesis—the following statement:

Localization-Topology Correspondence: *Consider a gapped periodic (magnetic) Schrödinger operator. Then it is always possible to construct a system*

[2]A remarkable exception is the well-known Landau Hamiltonian. Notice, however, that if a periodic background potential is included in the model, one is generically back to the absolutely-continuous setting.

$w = (w_1, \dots, w_m)$ of CWFs for the occupied states such that

$$\sum_{a=1}^{m} \int_{\mathbb{R}^d} |x|^{2s} \, |w_a(x)|^2 \mathrm{d}x < +\infty \qquad \textit{for every } s < 1. \tag{1}$$

Moreover, the following statements are equivalent:

(a) **Finite second moment:** *there exists a choice of Bloch gauge such that the corresponding CWFs $w = (w_1, \dots, w_m)$ satisfy*

$$\langle X^2 \rangle_w = \sum_{a=1}^{m} \int_{\mathbb{R}^d} |x|^2 \, |w_a(x)|^2 \mathrm{d}x < +\infty;$$

(b) **Exponential localization:** *there exists $\alpha > 0$ and a choice of Bloch gauge such that the corresponding CWFs $\widetilde{w} = (\widetilde{w}_1, \dots, \widetilde{w}_m)$ satisfy*

$$\sum_{a=1}^{m} \int_{\mathbb{R}^d} \mathrm{e}^{2\beta|x|} \, |\widetilde{w}_a(x)|^2 \mathrm{d}x < +\infty \qquad \textit{for every } \beta \in [0, \alpha);$$

(c) **Trivial topology:** *the Bloch bundle associated to the occupied states is trivial.*

Our result can be reformulated in terms of the localization functional introduced by Marzari and Vanderbilt [7, 8], which with our notation reads

$$\begin{aligned} F_{\mathrm{MV}}(w) &= \sum_{a=1}^{m} \int_{\mathbb{R}^d} |x|^2 |w_a(x)|^2 \, \mathrm{d}x - \sum_{a=1}^{m} \sum_{j=1}^{d} \left(\int_{\mathbb{R}^d} x_j |w_a(x)|^2 \, \mathrm{d}x \right)^2 \\ &=: \langle X^2 \rangle_w - \langle X \rangle_w^2. \end{aligned} \tag{2}$$

In view of the first part of the statement, there always exists a system of CWFs satisfying (1) for fixed $s = 1/2$, so that the first moment $\langle X \rangle_w$ is finite. Hence, the Marzari-Vanderbilt functional is finite if and only if $\langle X^2 \rangle_w$ is. By the second part of the Localization-Topology Correspondence, the latter condition is equivalent to the triviality of the Bloch bundle. The result is in agreement with previous numerical and analytic investigations on the Haldane model [13], and with more recent investigations on the subject [2]. As a consequence, the minimization of F_{MV} is possible only in the topologically trivial case, and numerical simulations in the topologically non-trivial regime should be handled with care: we expect that the numerics become unstable when the mesh in k-space becomes finer and finer [2].

Future possible applications of the Localization-Topology Correspondence go beyond the realm of crystalline solids, including superfluids and superconductors [11, 16], and tensor network states [12]. In view of that, we hope that our results will trigger new developments in the theory of superconductors and of many-body systems, and possibly in other areas of physics.

References

[1] A. J. Bestwick, E. J. Fox, X. Kou, L. Pan, K. L. Wang and D. Goldhaber-Gordon, *Precise quantization of the anomalous Hall effect near zero magnetic field*, Phys. Rev. Lett., **114**, 187201, (2015).

[2] E. Cancès, A. Levitt, G. Panati and G. Stoltz, *Robust determination of maximally-localized Wannier functions*, Phys. Rev. B, **95**, 075114, (2017).

[3] C. Z. Chang et al., *High-precision realization of robust quantum anomalous Hall state in a hard ferromagnetic topological insulator*, Nature Materials, **14**, 473, (2015).

[4] D. Fiorenza, D. Monaco and G. Panati, *Construction of real-valued localized composite Wannier functions for insulators*, Ann. Henri Poincaré, **17**, pp. 63–97, (2016).

[5] F. D. M. Haldane, *Model for a Quantum Hall effect without Landau levels: condensed-matter realization of the "parity anomaly"*, Phys. Rev. Lett., **61**, 2017, (1988).

[6] M. Z. Hasan and C. L. Kane, *Colloquium: Topological Insulators*, Rev. Mod. Phys., **82**, pp. 3045–3067, (2010).

[7] N. Marzari and D. Vanderbilt, *Maximally localized generalized Wannier functions for composite energy bands*, Phys. Rev. B, **56**, pp. 12847–12865, (1997).

[8] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza and D. Vanderbilt, *Maximally localized Wannier functions: Theory and applications*, Rev. Mod. Phys., **84**, 1419, (2012).

[9] D. Monaco, G. Panati, A. Pisante and S. Teufel, *Optimal decay of Wannier functions in Chern and Quantum Hall insulators*, Commun. Math. Phys., **359**, pp. 61–100, (2018).

[10] G. Panati and A. Pisante, *Bloch bundles, Marzari-Vanderbilt functional and maximally localized Wannier functions*, Commun. Math. Phys., **322**, pp. 835–875, (2013).

[11] S. Peotta and P. Törma *Superfluidity in topologically nontrivial flat bands*, Nature Commun., **8**, 8944, (2015).

[12] N. Read, *Compactly-supported Wannier functions and algebraic K-theory*, Phys. Rev. B, **95**, 115309, (2017).

[13] T. Thonhauser and D. Vanderbilt, *Insulator/Chern-insulator transition in the Haldane model*, Phys. Rev. B, **74**, 235111, (2006).

[14] D. J. Thouless, *Wannier functions for magnetic sub-bands*, J. Phys. C, **17**, pp. L325–L327, (1984).

[15] D. J. Thouless, M. Kohmoto, M. P. Nightingale and M. den Nijs, *Quantized Hall conductance in a two-dimensional periodic potential*, Phys. Rev. Lett., **49**, pp. 405–408, (1982).

[16] M. Tovmasyan, S. Peotta, P. Törma and S. D. Huber, *Effective theory and emergent $SU(2)$ symmetry in the flat bands of attractive Hubbard models*, Phys. Rev. B, **94**, 245149, (2016).

A classical statistical mechanics approach to understanding Green's function methods and the Luttinger-Ward formalism

Michael Lindsey

(joint work with Lin Lin)

The Luttinger-Ward (LW) formalism [1] is an important component of Green's function theories in quantum many-body physics. The LW functional $\Phi[G]$ provides the formal foundation for bold diagrammatic perturbation theory to all orders and is used to formally derive widely used numerical schemes such as the self-consistent Hartree-Fock approximation, the GW approximation [2], the dynamical mean-field theory (DMFT) [3, 4], and a number of its recent extensions such as the DMFT+GW method [5] and the dynamical cluster approximation [6].

Nonetheless, the very existence of the LW functional is currently under debate, with theoretical and numerical evidence favoring the contrary in the past few years for fermionic systems [7, 8, 9, 10]. Such failure has profound theoretical and practical implications. It suggests that many practically used Green's function methods for computing static or dynamic properties might fail in unpredictable ways. In particular, even in the perturbative regime where bare diagrams converge, the bold diagrams may fail to converge or converge to the wrong quantity [7].

In this talk, we provide the first rigorously justified LW formalism, in the context of classical statistical mechanics, or Euclidean lattice field theory (such as the φ^4 theory [11, 12]). Due to an exact correspondence between the Feynman diagrammatic expansion of lattice field theory and that of quantum many-body physics [13, 11], Euclidean lattice field theory retains the valuable structural information of diagrammatic expansions. Meanwhile, it avoids a key theoretical challenge of the fermionic setup, in the sense that the Green's function in the Euclidean lattice field theory, defined as a two-point correlator function, has a clearly defined domain, namely the set of positive definite matrices. Hence this work represents a key step towards understanding and potentially remedying the LW formalism and Green's function methods for fermionic systems. Our theory also proves for the first time the widely used bold diagrammatic expansion, interpreted as an asymptotic series for approximating the LW functional. Independently, our adaptation of the LW formalism to a new setting may provide new insight into the study of Euclidean field theories.

The material discussed in this talk is available in [14], and more detail from the mathematical perspective will be provided in future publications.

References

[1] J. M. Luttinger and J. C. Ward, *Ground-state energy of a many-fermion system. II*, Phys. Rev., **118** (1960), p. 1417.

[2] L. Hedin, *New method for calculating the one-particle Green's function with application to the electron-gas problem*, Phys. Rev., **139** (1965), p. A796.

[3] A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, *Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions*, Rev. Mod. Phys., **68** (1996), p. 13.

[4] M. Potthoff, *Non-perturbative construction of the Luttinger-Ward functional*, Condens. Matter Phys., **9** (2006), pp. 557–567.

[5] S. Biermann, F. Aryasetiawan and A. Georges, *First-principles approach to the electronic structure of strongly correlated systems: Combining the GW approximation and dynamical mean-field theory*, Phys. Rev. Lett., **90** (2003), p. 086402.

[6] P. Staar, T. Maier and T. C. Schulthess, *Dynamical cluster approximation with continuous lattice self-energy*, Phys. Rev. B, **88** (2013), p. 115101.

[7] E. Kozik, M. Ferrero and A. Georges, *Nonexistence of the Luttinger-Ward Functional and Misleading Convergence of Skeleton Diagrammatic Series for Hubbard-Like Models*, Phys. Rev. Lett., **114** (2015), p. 156402

[8] R. Elder, *Comment on "Non-existence of the Luttinger-Ward functional and misleading convergence of skeleton diagrammatic series for Hubbard-like models"*, arXiv:1407.6599, (2014).

[9] W. Tarantino, P. Romaniello, J. A. Berger and L. Reining, *Self-consistent Dyson equation and self-energy functionals: An analysis and illustration on the example of the Hubbard atom*, Phys. Rev. B, **96** (2017), p. 045124.
[10] O. Gunnarsson, G. Rohringer, T. Schäfer, G. Sangiovanni and A. Toschi, *Breakdown of Traditional Many-Body Theories for Correlated Electrons*, Phys. Rev. Lett., **119** (2017), p. 056402.
[11] D. J. Amit and V. Martin-Mayor, *Field theory, the renormalization group, and critical phenomena: graphs to computers*, World Scientific Publishing Co Inc., 2005.
[12] J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, Clarendon Pr., 2002.
[13] A. L. Fetter and J. D. Walecka, *Quantum theory of many-particle systems*, Courier Corp., 2003.
[14] L. Lin and M. Lindsey, *Variational structure of Luttinger-Ward formalism and bold diagrammatic expansion for Euclidean lattice field theory*, Proc. Natl. Acad. Sci., **115** (2018), p. 2282.

Generalized Kohn-Sham iteration on Banach spaces

Andre Laestadius
(joint work with Markus Penz, Erik I. Tellgren, Michael Ruggenthaler, Simen Kvaal and Trygve Helgaker)

We here propose an infinite dimensional and general Kohn-Sham formulation on Banach spaces. Furthermore, a weak form of convergence by means of the Optimal Damping Algorithm is established.

Let X be a real Banach space and X^* its dual. It is here assumed that X is strictly convex and X^* is uniformly convex. For $x^* \in X^*$, define an energy functional $E : X^* \to \mathbb{R}$ and consider the variational problem of finding the system state $x \in X$ that corresponds to minimal energy of

$$E(x^*) = \inf\{\tilde{F}(x) + \langle x^*, x\rangle \mid x \in \tilde{X}\}. \tag{1}$$

The functional $\tilde{F}(x)$ stands for all energy contributions of internal effects, and $\langle x^*, x\rangle$ represents the potential energy that is seen as an external and controllable effect. The domain of $\tilde{F}$ is limited to a certain set of "physical" densities $\tilde{X}$ that by themselves usually do not form a linear space. It is here not given that $\tilde{F}$ is convex and weakly lower semicontinuous (l.s.c.). Instead (borrowing notation from density-functional theory) we introduce a universal Lieb-type functional [1],

$$\begin{aligned} &F : X \to \mathbb{R} \cup \{+\infty\}, \\ &F(x) = \sup\{E(x^*) - \langle x^*, x\rangle \mid x^* \in X^*\}. \end{aligned}$$

Now, such a functional is by construction convex and weakly l.s.c and has $F(x) = +\infty$ whenever $x \in X \setminus \tilde{X}$ (corresponding to "unphysical" densities). It is key here that the principal problem stays the same when switching from $\tilde{F}$ to F. To find the state x of minimal energy in (1) by just relying on F we have to determine

$$\arg\min\{F(x) + \langle x^*, x\rangle \mid x \in X\}. \tag{2}$$

We do not assume that F is differentiable. The aim is to obtain the ground-state energy $E(x^*)$ from (1) as well as a corresponding minimizer x from (2):

$$-x^* \in \underline{\partial} F(x), \quad x \in \overline{\partial} E(x^*).$$

To meet that end, we make use of the Moreau-Yosida regularization and follow [2] where this approach was applied to density-functional theory on Hilbert spaces. Set $\phi = \frac{1}{2}\|\cdot\|^2$ on both X and X^* and let $J : X \to X^*$ be the duality map. For f convex and weakly l.s.c., define

$$f_\varepsilon(x) = \inf\{f(y) + \varepsilon^{-1}\phi(x-y) \mid y \in X\}.$$

The infimum in the definition of f_ε is always uniquely attained. This unique minimizer for any given x gives rise to the definition of the so-called proximal mapping,

$$\mathrm{prox}_{\varepsilon f}(x) := \arg\min\{f(y) + \varepsilon^{-1}\phi(x-y) \mid y \in X\}.$$

Applying the Moreau-Yosida regularization to F gives a F_ε that is Fréchet differentiable and $\nabla F_\varepsilon(x) = \varepsilon^{-1} J(x - \mathrm{prox}_{\varepsilon f}(x))$. We moreover set

$$E_\varepsilon(x^*) = \inf\{F_\varepsilon(x) + \langle x^*, x\rangle \mid x \in X\}.$$

It then holds

$$E(x^*) = E_\varepsilon(x^*) + \varepsilon\phi(x^*).$$

The Kohn-Sham idea [3] is based on the study of a simpler problem. Assume the existence of a reference functional $\tilde{F}^0 : \tilde{X} \to \mathbb{R}$ that belongs to a so-called Kohn-Sham system that captures parts of the real system's internal physics. This leads to a variational problem that is supposedly easier to solve. Just like with $\tilde{F}$ we derive the regularized functionals F^0_ε and E^0_ε and set up the reference problem in analogous fashion

$$\begin{aligned} -{x_{\mathrm{KS}}}^* \in \nabla F^0_\varepsilon(x) &\iff x \in \overline{\partial} E^0_\varepsilon({x_{\mathrm{KS}}}^*), \\ -x^* \in \nabla F_\varepsilon(x) &\iff x \in \overline{\partial} E_\varepsilon(x^*). \end{aligned}$$

Note that the Kohn-Sham system and the real system yield the same state, i.e., the minimizer state x is the same in both cases. It is necessary to choose a different and at this stage completely undetermined potential for the reference system, the so-called Kohn-Sham potential ${x_{\mathrm{KS}}}^*$. We remark that the problem of "v-representability" plays no role in the regularized setting: By differentiability of F_ε and F^0_ε, potentials always exist

$${x_{\mathrm{KS}}}^* = -\nabla F^0_\varepsilon(x), \quad x^* = -\nabla F_\varepsilon(x).$$

To determine the Kohn-Sham potential we take the difference of ${x_{\mathrm{KS}}}^* = -\nabla F^0_\varepsilon(x)$ and $x^* = -\nabla F_\varepsilon(x)$, which yields the first step in a self-consistent iteration scheme. The next iteration step towards ${x_{\mathrm{KS}}}^*$ is then given by

$$x^*_{i+1} = x^* + \nabla F_\varepsilon(x_i) - \nabla F^0_\varepsilon(x_i).$$

Using the Optimal Damping Algorithm [4] we find the steepest descent direction of $F_\varepsilon(x) + \langle x^*, x\rangle$ and minimize $F_\varepsilon(x) + \langle x^*, x\rangle$ along this direction. Our main result is the following:

Theorem 1 (Regularized Kohn-Sham iteration)**.** *Set* $x_1^* = x^*$ *and solve* $x_1 \in \partial E_\varepsilon^0(x_1^*)$*. Iterate* $i = 1, 2, \ldots$ *according to:*

(*a*) $x_{i+1}^* = x^* + \nabla F_\varepsilon(x_i) - \nabla F_\varepsilon^0(x_i)$ *stop if* $x_{i+1}^* = -\nabla F_\varepsilon^0(x_i) = {x_{\mathrm{KS}}}^*$,

(*b*) *select* $\tilde{x}_{i+1} \in \partial E_\varepsilon^0(x_{i+1}^*)$,

(*c*) *choose* $t_i \in (0, 1]$ *maximally such that for* $x_{i+1} = x_i + t_i(\tilde{x}_{i+1} - x_i)$ *one has*

$$\langle \nabla F_\varepsilon(x_{i+1}) + x^*, \tilde{x}_{i+1} - x_i\rangle \leq 0.$$

The descending sequence $\{F_\varepsilon(x_i) + \langle x^*, x_i\rangle\}_i$ *converges as a sequence of real numbers to*

$$e_\varepsilon(x^*) = \inf_i \{F_\varepsilon(x_i) + \langle x^*, x_i\rangle\} \geq E_\varepsilon(x^*).$$

Thus, the shifted $e_\varepsilon(x^*) + \varepsilon\phi(x^*)$ *is an upper bound for the ground-state energy* $E(x^*)$*.*

References

[1] E. H. Lieb, *Density functionals for coulomb systems*, Int. J. Quant. Chem., **24** (3), 1983.

[2] S. Kvaal, U. Ekström, A. Teale and T. Helgaker, *Differentiable but exact formulation of density-functional theory*, J. Chem. Phys., **140**, 18A518 (2014).

[3] W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*, Phys. Rev., **140**, A1133 (1965).

[4] E. Cancès, *SCF algorithms for Kohn-Sham models with fractional occupation numbers*, J. Chem. Phys., **114**, 10616 (2001).

Tensor-based modelling of long range electrostatic potentials in many-particle systems

Venera Khoromskaia

The novel tensor-structured numerical methods appeared as a result of bridging of the algebraic tensor decompositions originating from chemometrics and of the non-linear approximation theory on separable representation of multivariate functions and operators [9]. The prior results on theory of the low-rank tensor-product approximation of multivariate functions and operators based, in particular, on *sinc*-quadrature techniques [4] were a significant background for the advanced approaches in scientific computing. The tensor numerical techniques are based on the representation of d-variate functions and operators on large $n^{\otimes d}$ grids in the rank-structured tensor formats which provide $O(dn)$ complexity of numerical calculations instead of $O(n^d)$ by conventional methods.

A starting point was the Hartree-Fock solver based on the tensor-structured calculation of the two-electron integrals, and of the Laplace and nuclear potential operators using a Gaussian-type basis, discretized on $n \times n \times n$ 3D Cartesian

grids [10, 7]. The tensor approach enables calculation of the 3D convolution integral operators in $O(n \log n)$ complexity, with the representation of the convolution kernel $\frac{1}{\|x\|}$, $x \in \mathbb{R}^3$ by a low-rank canonical tensor [8],

$$\mathbf{P}_R = \sum_{q=1}^{R} \mathbf{p}_q^{(1)} \otimes \mathbf{p}_q^{(2)} \otimes \mathbf{p}_q^{(3)} \in \mathbb{R}^{n \times n \times n}. \tag{1}$$

Thus for all operators in the non-linear 3D integro-differential Hartree-Fock equation the 3D analytical integration is completely avoided, since it is substituted by the grid-based tensor algorithms in 1D complexity.

Recently the rank-structured tensor approach suggested a progress in the numerical treatment of the long-range electrostatic potentials in many-particle systems. Let us consider a sum of single Coulomb potentials on a finite $L \times L \times L$ lattice in a volume box $\Omega_0 = [-b/2, b/2]^3$,

$$V_{c_L}(x) = \sum_{k_1,k_2,k_3 \in K} \frac{Z}{\|x - a_1(k_1,k_2,k_3)\|}, \quad x \in \Omega_L \in \mathbb{R}^3. \tag{2}$$

The assembled tensor summation method applies to the lattice potentials defined on $n \times n \times n$ 3D Cartesian grid. It reduces the calculation of the collective potential sum over a rectangular 3D lattice,

$$\mathbf{P}_{c_L} = \sum_{\mathbf{k} \in K^3} W_{\nu(\mathbf{k})} \widetilde{\mathbf{P}} = \sum_{k_1,k_2,k_3 \in K} \sum_{q=1}^{R} W_{(\mathbf{k})} (\widetilde{\mathbf{p}}_q^{(1)} \otimes \widetilde{\mathbf{p}}_q^{(2)} \otimes \widetilde{\mathbf{p}}_q^{(3)}) \in \mathbb{R}^{n \times n \times n},$$

to the summation (assembling) of shifted directional vectors of the canonical tensor representation for a single Newton kernel [5],

$$\mathbf{P}_{c_L} = \sum_{q=1}^{R} \Big(\sum_{k_1 \in K} W_{(k_1)} \widetilde{\mathbf{p}}_q^{(1)} \Big) \otimes \Big(\sum_{k_2 \in K} W_{(k_2)} \widetilde{\mathbf{p}}_q^{(2)} \Big) \otimes \Big(\sum_{k_3 \in K} W_{(k_3)} \widetilde{\mathbf{p}}_q^{(3)} \Big). \tag{3}$$

Here $\widetilde{\mathbf{P}}$ (similar to (1)) represents the single Newton kernel on a twice larger grid and $W_{\nu(\mathbf{k})} = W_{k_1} \otimes W_{k_2} \otimes W_{k_3}$ is the shift-and-windowing (onto Ω_L) separable transform along the $\mathbf{k}$-grid. For rectangular finite 3D lattices, the rank of the resulting sum is proven to be the same as for the R-term canonical reference tensor $\widetilde{\mathbf{P}}$ representing a single Coulomb potential. For lattices with multiple vacancies the tensor rank is increased by a small factor [6].

The numerical cost and storage size for 3D lattices are bounded by $O(RLn)$ and $O(Rn)$, respectively, where n is the univariate grid size. Figure 1 presents the assembled canonical vectors for the cluster of $16 \times 8 \times 2$ Hydrogen nuclei, with a distance 1.4 bohr between nuclei and the cross-section of its collective electrostatic potential.

The method of grid-based assembled tensor summation of the electrostatics potentials on $L \times L \times L$ finite lattices provides the computational complexity of the order of $O(L)$, and calculation of the interaction energy in $O(L^2)$ [7]. Note that the traditional approaches, like Ewald-type summation [3] exhibit $O(L^3)$ complexity.

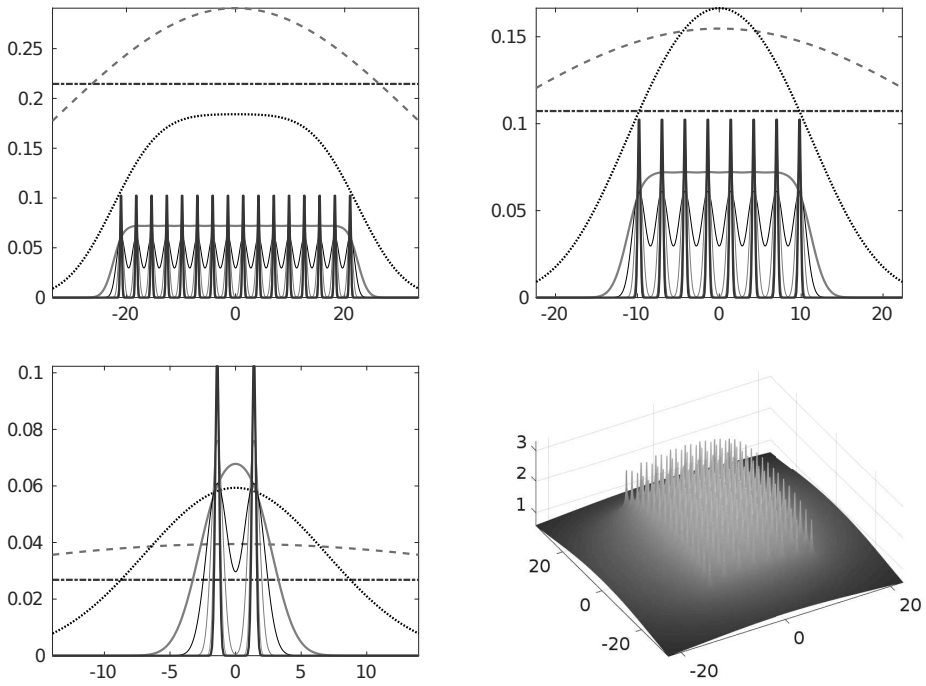


FIGURE 1. Assembled x-, y- and z-axis canonical vectors for a cluster of $16\times8\times2$ Hydrogen atoms and the collective electrostatic potential.

Recent range-separated (RS) tensor format introduced in [1] applies to many particle systems with rather generally located potentials. These can be the electrostatic potentials of large atomic systems like bio-molecules or the multidimensional scattered data modeled by radial basis functions. The main advantage of the RS tensor format is that the partition into the long- and short-range parts is performed just by sorting skeleton vectors in the tensor representation of the generating Newton kernel,

$$\mathbf{P}_R = \mathbf{P}_{R_s} + \mathbf{P}_{R_l}.$$

It was proven [1] that the sum of long range contributions from all particles in the collective potential is represented by a low-rank canonical/Tucker tensor with a rank which only logarithmically depends on the number of particles N. The representation complexity of the short range part is $O(N)$ with a small constant independent on the number of particles. The RS-canonical tensor format specifies the class of d-tensors $\mathbf{A} \in \mathbb{R}^{n_1\times\cdots\times n_d}$ which can be represented as a sum of a rank-R canonical tensor $\mathbf{U} = \sum_{k=1}^{R} \xi_k \mathbf{u}_k^{(1)} \otimes \cdots \otimes \mathbf{u}_k^{(d)} \in \mathbb{R}^{n_1\times\cdots\times n_d}$ and a (uniform) cumulated canonical tensor $\widehat{\mathbf{U}} = \sum_{\nu=1}^{N} c_\nu \mathbf{U}_\nu$ generated by $\mathbf{U}_0$ with $\mathrm{rank}(\mathbf{U}_0) \le R_0$,

$$\mathbf{A} = \sum\nolimits_{k=1}^{R} \xi_k \mathbf{u}_k^{(1)} \otimes \cdots \otimes \mathbf{u}_k^{(d)} + \sum\nolimits_{\nu=1}^{N} c_\nu \mathbf{U}_\nu. \tag{4}$$

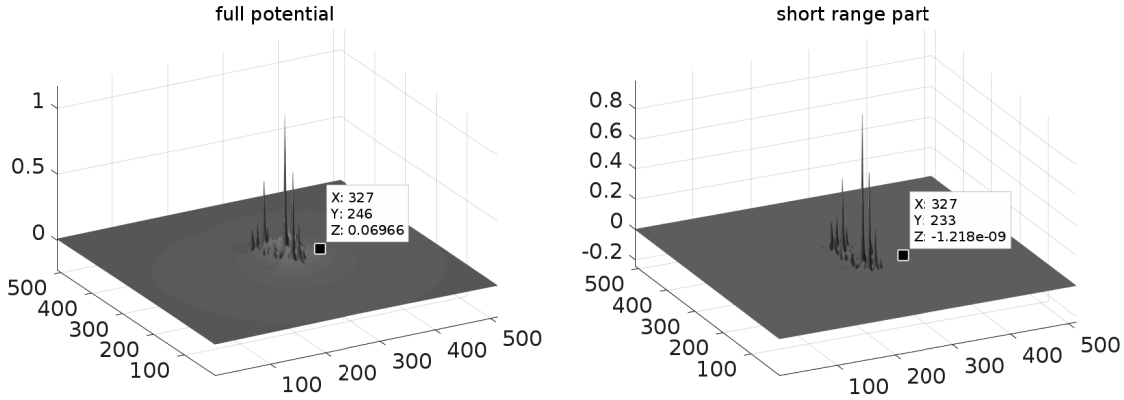


FIGURE 2. Left: the free space electrostatic potential of a small biomolecule computed by RS tensor format. Right: the short-range part of the RS tensor.

The basic tools here are the canonical-to-Tucker algorithm and the reduced higher order SVD (RHOSVD) introduced in [10]. The error of the RS tensor representation is defined by the ε-truncation threshold for the Tucker-to-canonical algorithm in the rank reduction scheme. Figures 2 and 3 illustrate the cross-sections of the collective free space electrostatic potential for the 379 atomic biomolecule [2] computed by the RS tensor representation.

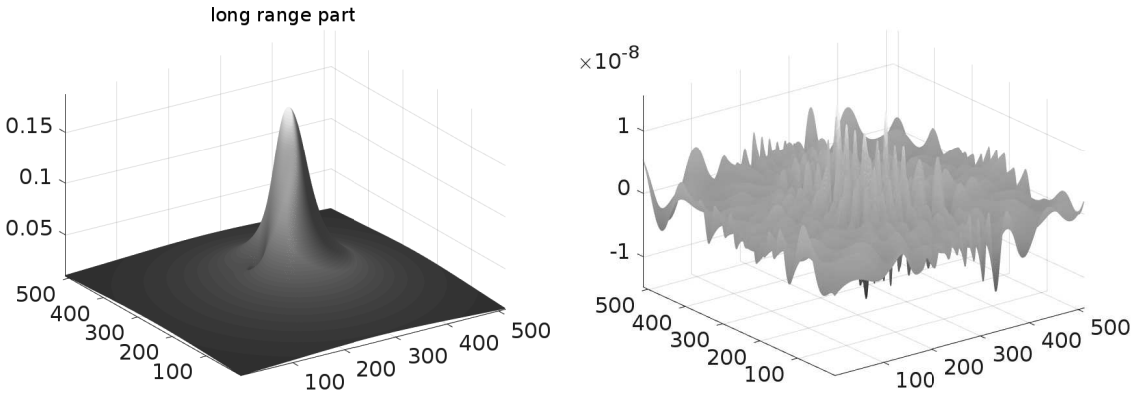


FIGURE 3. The long-range part of the collective free space electrostatic potential of a small biomolecule (left) and the error of RS representation (right).

REFERENCES

[1] P. BENNER, V. KHOROMSKAIA AND B. N. KHOROMSKIJ, *Range-Separated Tensor Format for Many-Particle Modeling*, SIAM J. Sci. Comp., **40** (2), pp. A1034–A1062, 2018.

[2] P. BENNER, V. KHOROMSKAIA, B. N. KHOROMSKIJ, C. KWEYU AND M. STEIN, *Regularization of the Poisson-Boltzmann equation by using the range-separated tensor format*, Manuscript, 2018.

[3] P.P. Ewald, *Die Berechnung optische und elektrostatischer Gitterpotentiale*, Ann. Phys **64**, 253 (1921).
[4] I. P. Gavrilyuk, W. Hackbusch and B. N. Khoromskij, *Data-Sparse Approximation to Operator-Valued Functions of Elliptic Operator*, Math. Comp. **73**, (2003), pp. 1297–1324.
[5] V. Khoromskaia and B. N. Khoromskij, *Grid-based Lattice Summation of Electrostatic Potentials by Assembled Rank-structured Tensor Approximation*, Comp. Phys. Comm., **185**, 2014, pp. 3162–3174.
[6] V. Khoromskaia and B. N. Khoromskij, *Fast tensor method for summation of long-range potentials on 3D lattices with defects*, Numer. Lin. Algebra Appl., **23**, pp. 249–271, 2016.
[7] V. Khoromskaia and B. N. Khoromskij, *Tensor Numerical Methods in Quantum Chemistry: from Hartree-Fock to Excitation Energies*, Phys. Chemistry Chem. Physics, 2015, **17**, pp. 31491–31509.
[8] B. N. Khoromskij, *Fast and Accurate Tensor Approximation of a Multivariate Convolution with Linear Scaling in Dimension*, J. Comp. Appl. Math., **234** (2010), pp. 3122–3139.
[9] B. N. Khoromskij, *Tensor Numerical Methods in Scientific Computing*, Research monograph, De Gruyter Verlag, Berlin, 2018.
[10] B. N. Khoromskij and V. Khoromskaia, *Multigrid Tensor Approximation of Function Related Arrays*, SIAM J. Sci. Comput., **31** (4), pp. 3002–3026, 2009.

New directions in coupled-cluster theory

Thomas Bondo Pedersen

(joint work with Gustav Baardsen, Audun Skau Hansen, Karl R. Leikanger, Elisa Rebolini, Lorenzo Maschio and Simen Kvaal)

While not the most widely used electronic-structure theory—a position held firmly by Kohn-Sham density-functional theory, coupled-cluster (CC) theory is the high-accuracy method of choice for systems dominated by a single electronic configuration and is colloquially referred to as the "gold standard" in the quantum chemistry community. The application of CC theory, however, has been restricted to stationary electronic states of finite molecular systems. It is perfectly reasonable to expect CC theory to excel at describing stationary states of extended systems and for electron dynamics.

Although CC theory exhibits a benign polynomial-scaling computational cost relative to the factorial scaling of full configuration interaction, it is still too expensive for straightforward application to extended systems. We have recently generalized the linear-scaling divide-expand-consolidate (DEC) approach to ground-state correlation energies developed for molecules by Jørgensen and coworkers [1, 2, 3] to extended systems with periodic boundary conditions [4]. The extended DEC (X-DEC) framework attempts to exploit the short-ranged nature of electron correlation in gapped systems using a basis of well-localized (generalized) Wannier functions spanning both the occupied and the unoccupied single-particle spaces. Assigning each Wannier function, unoccupied as well as occupied, to an atomic site A, the CC correlation energy per unit cell may be written as a sum of atomic site energies E_A in the central unit cell and interaction energies ΔE_{AB} between

the central unit cell sites and all other sites:

$$E_{\mathrm{corr}} = \sum_{A} E_A + \sum_{B<A} \Delta E_{AB} \tag{1}$$

$$E_A = \sum_{ij\in A} \sum_{ab} E_{ij}^{ab} \tag{2}$$

$$\Delta E_{AB} = \Big(\sum_{\substack{i\in A \\ j\in B}} + \sum_{\substack{i\in B \\ j\in A}} \Big) \sum_{ab} E_{ij}^{ab} \tag{3}$$

$$E_{ij}^{ab} = \left(t_{ij}^{ab} - t_i^a t_j^b\right) (ia|jb) \tag{4}$$

$$(ia|jb) = \iint \psi_i(r)\psi_a(r)|r-r'|^{-1}\psi_j(r')\psi_b(r')\ \mathrm{d}r'\mathrm{d}r \tag{5}$$

where t_i^a and t_{ij}^{ab} are single- and double-excitation amplitudes. While this expression is exact, the X-DEC approximation attempts to exploit the fast asymptotic decay of the electron repulsion integrals ($(ia|jb) \sim O(R^{-6})$) to truncate summations and thus make calculations feasible. Error control is obtained by solving amplitude equations in systematically increased orbital subspaces for each site A until E_A is stable within a predefined tolerance. The converged orbital subspaces are then used for each significant pair A, B to solve for pair amplitudes required to compute ΔE_{AB}. Since all fragment calculations are independent, this not only leads to linear-scaling complexity but also allows for an embarrassingly parallel implementation.

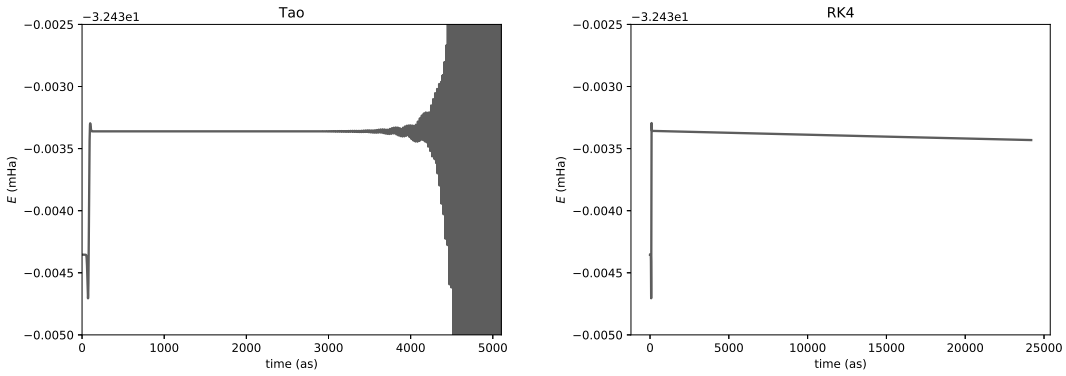
Intuitively, one would expect the performance of the X-DEC scheme to improve with increased locality of the Wannier functions. In [4], however, we observed that the orbital subspaces used for solving the atomic site amplitude equations are surprisingly large, limiting the computational performance of the method. To investigate this problem further, we have used the local-correlation algorithm implemented in the Cryscor program [5] to test the convergence of the second-order Møller-Plesset correlation energy with respect to excitation domain size, comparing unoccupied Wannier functions with projected atomic orbitals (PAOs). The PAOs are obtained by projecting out the occupied states from the atomic-orbital basis functions, thus creating a linearly dependent nonorthonormal set that spans the unoccupied orbital space but having significantly greater spread (less locality) than the linearly independent orthonormal Wannier functions spanning the same space. Preliminary results for bulk LiH show that the correlation energy is converged to within 1 mHa using the PAOs on the 6 nearest-neighbor sites only. With unoccupied Wannier functions, however, a domain size comprising 32 atoms (up to fourth-nearest neighbor sites) is required to achieve milli-Hartree accuracy of the correlation energy. From a local correlation perspective, therefore, the requirement that Wannier functions decay exponentially at infinite distance is necessary but not sufficient. Defining a localization functional that leads to a set of unoccupied Wannier functions with exponential asymptotic decay and, simultaneously, captures as much of the correlation energy with as few functions as possible is a subject for further research.

Going beyond the calculation of stationary electronic states, solving the time-dependent CC equations paves the way for highly accurate studies of atto-second processes in strong laser pulses as well as (nonperturbative) treatments of conventional molecular response properties in the frequency domain through Fourier transformations. Relatively little work has been done in this direction [6, 7, 8, 9] and the first step is the integration of the time-dependent CC equations, which are complex analogues of Hamilton's equations of classical mechanics [10],

$$\dot{t} = -i\frac{\partial \mathcal{H}}{\partial \lambda}(t) \tag{6}$$

$$\dot{\lambda} = i\frac{\partial \mathcal{H}}{\partial t}(t, \lambda) \tag{7}$$

where t and λ are amplitude vectors. With the linear parameterization chosen here, λ becomes the (time-dependent) Lagrange multipliers of Helgaker and Jørgensen [11]. The Hamiltonian $\mathcal{H}$ is nonseparable and due to the high computational cost of evaluating the derivatives on the right-hand side, we have tested the *explicit* symplectic second-order integrator recently proposed by Tao [12], aiming at long-time stability with (relatively) large time steps. For the He atom exposed to a uniform electric-field with maximum amplitude at 72 as, however, we find that the Tao integrator diverges with time steps above approximately 2.4 as. For comparison, the fourth-order Runge-Kutta method shows a less dramatic drift in energy.



References

[1] M. Ziółkowski, B. Jansík, T. Kjærgaard and P. Jørgensen, *Linear scaling coupled cluster method with correlation energy based error control*, J. Chem. Phys., **133** (2010), 014107.

[2] K. Kristensen, M. Ziółkowski, B. Jansík, T. Kjærgaard and P. Jørgensen, *A Locality Analysis of the Divide–Expand-Consolidate Coupled Cluster Amplitude Equations*, J. Chem. Theory Comput., **7** (2011), pp. 1677–1694.

[3] I.-M. Høyvik, K. Kristensen, B. Jansík and P. Jørgensen, *The divide-expand-consolidate family of coupled cluster methods*, J. Chem. Phys., **136** (2012), 014105.

[4] E. Rebolini, G. Baardsen, A. S. Hansen, K. R. Leikanger and T. B. Pedersen, *Divide-Expand-Consolidate Second-Order Møller-Plesset Theory with Periodic Boundary Conditions*, J. Chem. Theory Comput. In press (2018). DOI: 10.1021/acs.jctc.8b00021

[5] C. Pisani, M. Schütz, S. Casassa, D. Usvyat, L. Maschio, M. Lorenz and A. Erba, *Cryscor: a program for the post-Hartree-Fock treatment of periodic systems*, Phys. Chem. Chem. Phys., **14** (2012), pp. 7615–7628.
[6] S. Kvaal, *Ab initio quantum dynamics using coupled-cluster*, J. Chem. Phys., **136** (2012), 194109.
[7] D. R. Nascimento and A. E. DePrince III, *Linear Absorption Spectra from Explicitly Time-Dependent Equation-of-Motion Coupled-Cluster Theory*, J. Chem. Theory Comput., **12** (2016), pp. 5834–5840.
[8] D. R. Nascimento and A. E. DePrince III, *Simulation of Near-Edge X-ray Absorption Fine Structure with Time-Dependent Equation-of-Motion Coupled-Cluster Theory*, J. Phys. Chem. Lett., **8** (2017), pp. 2951–2957.
[9] T. Sato, H. Pathak, Y. Orimo and K. L. Ishikawa, *Time-dependent optimized coupled-cluster method for multielectron dynamics*, J. Chem. Phys., **148** (2018), 051101.
[10] T. B. Pedersen and H. Koch, *On the time-dependent Lagrangian approach in quantum chemistry*, J. Chem. Phys., **108** (1998), pp. 5194–5204.
[11] T. Helgaker and P. Jørgensen, *Calculation of geometrical derivatives in molecular electronic structure theory*, Methods in Computational Molecular Physics, S. Wilson and G. H. F. Diercksen (Eds.), Plenum, New York (1992), pp. 353–421.
[12] M. Tao, *Explicit symplectic approximation of nonseparable Hamiltonians: Algorithm and long time performance*, Phys. Rev. E, **94** (2016), 043303.

Optimization of the first bands of a Hill's operator

Virginie Ehrlacher
(joint work with Athmane Bakhta, David Gontier)

The aim of this talk was to present some new considerations on the problem of optimizing the first bands of a periodic Hill's operator, motivated by materials design applications. The question can be stated as follows: given M functions defined on $(-1/2, 1/2)$, denoted by $b_1, \dots, b_M$, is it possible to find an optimal periodic potential V which minimizes the functional

$$\sum_{m=1}^{M} \int_{-1/2}^{1/2} \left| b_m(q) - \epsilon_{m,q}^V \right|^2 \, dq$$

where $(-1/2, 1/2) \ni q \mapsto \epsilon_{m,q}^V$ is the m^{th} band of the 2π-periodic Hill's operator $-\frac{1}{2}\partial_{xx} + V$.

It is possible to rigorusly prove an existence result for the optimization of the first band ($M = 1$) provided that the optimal potential V is searched for in a particular class of singular potentials (Borle measures). Several numerical methods can be proposed for the resolution of the above mentioned optimization problem in practice.

A Numerical Linear Algebra Perspective of Projection-based Embedding Theory

Leonardo Zepeda-Núñez
(joint work with Lin Lin)

Solving the many body Schrödinger equation, even in its approximate form, can be very challenging when the system size becomes large. Under certain circumstances, large quantum systems can be partitioned into two parts: the "system" (or "defect'") part containing the degrees of freedom of interest, which need to be treated accurately, and a "bath" (or "environment") part containing the remaining degrees of freedom that can be treated approximately. In these cases, it naturally becomes desirable to have a numerical method that can restrict the calculation to the system part only, resulting in a much lower computational cost. This intuitive idea has led to the development of various "quantum embedding theories" [3, 2] in which different models have been coupled together resulting in cheaper methods.

We focus on the quantum embedding theory within the context of Kohn-Sham density functional theory (KSDFT). In particular, we focus on the recently developed Projection-based Embedding Theory (PET) [1], which we reformulate within the formalism of linear algebra, and extend using a perturbation argument.

After proper discretization, KSDFT can be represented as the following nonlinear eigenvalue problem

$$H[P]\Psi = \Psi\Lambda, \quad P = \Psi\Psi^*, \tag{1}$$

where $H[P] \in \mathbb{C}^{N\times N}$ is a Hermitian matrix. To solve this problem, we need to compute the algebraically lowest N_e eigenvalues encoded in the diagonal matrix $\Lambda \in \mathbb{R}^{N_e\times N_e}$ and the associated eigenvectors $\Psi \in \mathbb{C}^{N\times N_e}$, which satisfy the orthonormality condition $\Psi^*\Psi = I_{N_e}$. P is a spectral projector, usually called the *density matrix*. The Hamiltonian $H[P]$ depends nonlinearly on the density matrix P, and (1) needs to be solved self-consistently.

We are mainly interested in the accurate computation of the block of P corresponding to the system part, thus sharply reducing the computation cost.

To reformulate the PET within the context of linear algebra, we start with the linear case. Within the linear regime, $H[P] = H \in \mathbb{C}^{N\times N}$ is a Hermitian matrix, whose eigenvalues are ordered non-decreasingly as $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_{N_e} < \lambda_{N_e+1} \leq \cdots \leq \lambda_N$, and we assume that there is a positive energy gap between the N_e-th and (N_e+1)-th eigenvalues. Then (1) is the Euler-Lagrange equation of the following energy minimization problem

$$E = \inf_{\substack{P^2=P, P^*=P \\ \mathrm{Tr}P=N_e}} \mathcal{E}[P], \text{ where } \mathcal{E}[P] := \mathrm{Tr}[HP], \tag{2}$$

where the condition $P = P^2$ requires P to be a projector.

In addition, let $H_0 \in \mathbb{C}^{N\times N}$ be a reference Hamiltonian, and P_0 to be the known minimizer of

$$E_0 = \inf_{\substack{P^2=P, P^*=P \\ \mathrm{Tr}P=N_e^0}} \mathrm{Tr}[H_0 P]. \tag{3}$$

Within this context, PET efficiently computes an approximation to P by leveraging knowledge of P_0, under the assumption that the density matrices P and P_0 do not differ much in the bath. This can be encoded by splitting P_0 as

$$P_0 = P_{0,b} + P_{0,s}. \tag{4}$$

where $P_{0,b}$ and $P_{0,s}$ are both projectors and orthogonal to each other, and by assuming that P can be approximately split in a similar fashion. These assumptions lead to the PET ansatz to the density matrix:

$$P \approx P^{\mathrm{PET}} = P_{0,b} + P_s, \tag{5}$$

where $P_s^2 = P_s$ is also a projector and it is orthogonal to $P_{0,b}$. Since the rank of $P_{0,b}$ is already N_b, the rank of P_s is thus equal to $N_s := N_e - N_b$.

Thus for the linear problem, PET solves the following constrained minimization problem with respect to P_s:

$$E^{\mathrm{PET}} = \inf_{\substack{P_s^2=P_s, P_s^*=P_s \\ P_{0,b}P_s=0, \mathrm{Tr}P_s=N_s}} \mathrm{Tr}[H(P_s + P_{0,b})]. \tag{6}$$

Compared to (2), we find that PET restrains the domain of the density matrices only to those satisfying the ansatz (5). Hence by the variational principle $E^{\mathrm{PET}} \geq E$ provides an upper bound for the energy. Computationally, PET reduces the number of eigenpairs that need to be computed in the eigenvalue problem from N_e to N_s.

Note that the dimension of H_0 and H must be the same, but N_e^0 and N_e can be different, and thus the ranks of $P_{0,s}$ and P_s can also be different. This is necessary in the context of KSDFT, where the system part in H can involve different numbers and/or types of atoms from that in H_0.

In order to compute the minimizer to (6), we define the deflated Hamiltonian, $H|_{\mathcal{B}_0^\perp} = (I - P_{0,b})H(I - P_{0,b})$, to be the restriction of H to the subspace orthogonal to the range of $P_{0,b}$, which we denote by $\mathcal{B}_0$, and assume that there is a positive gap between the N_s-th and (N_s+1)-th eigenvalue of $H|_{\mathcal{B}_0^\perp}$. Then the variational problem (6) has a unique minimizer, which is given by the solution to the following linear eigenvalue problem

$$H|_{\mathcal{B}_0^\perp}\Psi_s = \Psi_s\Lambda_s, \quad P_s = \Psi_s\Psi_s^*, \tag{7}$$

where (Ψ_s, Λ_s) are the lowest N_s eigenpairs of $H|_{\mathcal{B}_0^\perp}$.

We show that PET can be understood as an eigenvalue problem of a matrix whose off-diagonal blocks are neglected, resulting in solving two decoupled eigenvalue problems: one involving only the bath, and the other involving the system, as shown in (7). In order to uncover the structure of the problem, we conceptually

define a unitary $N \times N$ matrix $W := [\Psi_{0,b}, \Psi_s, \Psi_u]$, where $\Psi_{0,b}$ is an orthogonal matrix in the range of $P_{0,b}$ such that $\Psi_{0,b} H_0 \Psi_{0,b} = \Lambda_{0,b}$ and $P_{0,b} = \Psi_{0,b}\Psi_{0,b}^*$, Ψ_s is the solution to (7), and Ψ_u are the unoccupied eigenvectors in (7).

The matrix representation of H with respect to the basis W, denoted by H_W, can be written as

$$\begin{aligned} H_W = W^* H W &= \begin{bmatrix} \Psi_{0,b}^* H \Psi_{0,b} & \Psi_{0,b}^* H \Psi_s & \Psi_{0,b}^* H \Psi_u \\ \Psi_s^* H \Psi_{0,b} & \Psi_s^* H \Psi_s & \Psi_s^* H \Psi_u \\ \Psi_u^* H \Psi_{0,b} & \Psi_u^* H \Psi_s & \Psi_u^* H \Psi_u \end{bmatrix}, \\ &= \begin{bmatrix} \Psi_{0,b}^* H \Psi_{0,b} & \Psi_{0,b}^* H \Psi_s & \Psi_{0,b}^* H \Psi_u \\ \Psi_s^* H \Psi_{0,b} & \Lambda_s & 0 \\ \Psi_u^* H \Psi_{0,b} & 0 & \Lambda_u \end{bmatrix}. \end{aligned}$$

where we used the orthogonality of Ψ_s and Ψ_u, and Λ_u is a diagonal matrix with the unoccupied eigenvalues of (7) in its diagonal. Computing the eigen-decomposition of H_W would yield the exact answer to (2). Instead, PET computes an eigen-decomposition of an auxiliary matrix H_W^{PET}. In particular, PET performs two approximations: first, it discards all the off-diagonal blocks, and second, in the first diagonal term it approximates $H = H_0 + \Delta H$, by H_0, which leads to

$$H_W^{\mathrm{PET}} = \begin{bmatrix} \Lambda_{0,b} & 0 & 0 \\ 0 & \Lambda_s & 0 \\ 0 & 0 & \Lambda_u \end{bmatrix} = \begin{bmatrix} \Psi_{0,b}^* H_0 \Psi_{0,b} & 0 & 0 \\ 0 & \Lambda_s & 0 \\ 0 & 0 & \Lambda_u \end{bmatrix} \approx \begin{bmatrix} \Psi_{0,b}^* H \Psi_{0,b} & 0 & 0 \\ 0 & \Lambda_s & 0 \\ 0 & 0 & \Lambda_u \end{bmatrix}.$$

PET can be recast as solving an optimization problem using H_W^{PET}, whose minimizer, under certain gap conditions, is given by

$$P_W^{\mathrm{PET}} = \begin{bmatrix} I_{N_b} & 0 & 0 \\ 0 & I_{N_s} & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

When rotated back to the standard basis, the density matrix becomes

$$P^{\mathrm{PET}} = W P_W^{\mathrm{PET}} W^* = \Psi_{0,b}\Psi_{0,b}^* + \Psi_s \Psi_s^* = P_{0,b} + P_s.$$

Using this formalism we can define a perturbation of $P = P^{\mathrm{PET}} + \delta P$, where δP is computed from the perturbation

$$\delta H_W = H_W - \Delta H_W = \begin{bmatrix} \Psi_{0,b}^* \Delta H \Psi_{0,b} & \Psi_{0,b}^* H \Psi_s & \Psi_{0,b}^* H \Psi_u \\ \Psi_s^* H \Psi_{0,b} & 0 & 0 \\ \Psi_u^* H \Psi_{0,b} & 0 & 0 \end{bmatrix}.$$

Using the structure of δH_W, the Dyson equation, and the Cauchy integral formula, we can deduce an expression of δP, which is given by:

$$\delta P = \delta\Psi_{0,b}\Psi_{0,b}^* + \text{h.c.} \tag{8}$$

where $\delta\Psi_{0,b} \in \mathbb{C}^{N \times N_b}$ satisfies the equation

$$Q\left(\lambda_{i;0,b} I - H\right) Q \delta\psi_{i;0,b} = Q(H\psi_{i;0,b}), \quad Q\delta\psi_{i;0,b} = \delta\psi_{i;0,b}. \tag{9}$$

Here the projector $Q = I - (P_s + P_{0,b}) = \Psi_u \Psi_u^*$. $\lambda_{i;0,b}$ is the i-th diagonal element of $\Lambda_{0,b}$. $\psi_{i;0,b}$, and $\delta\psi_{i;0,b}$ are the i-th columns of $\Psi_{0,b}$, and $\delta\Psi_{0,b}$, respectively. h.c. represents for the Hermite conjugation of the first term.

Even though the theory for the linear problem seems to be rather complete, its extension to the non-linear case remains mostly unexplored. From a algorithmic point of view, formulating the PET as a variational problem makes the extension of the algorithm to the nonlinear case seamless. Consider a more general energy functional such as

$$\mathcal{E}[P] = \mathrm{Tr}[PH_L] + E_{\mathrm{Hxc}}[P], \tag{10}$$

where H_L is a given matrix derived from the discretized Laplacian operator and the electron-nuclei interaction potential. $E_{\mathrm{Hxc}}[P]$ is a nonlinear functional of the density matrix P, and it consists of the Hartree, and exchange correlation energy.

In such case, the minimization problem can be stated as (2), whose Euler-Lagrange equation is precisely (1), which in this case takes the form

$$H[P]\Psi = (H_L + V_{\mathrm{Hxc}}[P])\Psi = \Psi\Lambda, \quad P = \Psi\Psi^*, \tag{11}$$

where $V_{\mathrm{Hxc}}[P] = \frac{\delta E_{\mathrm{Hxc}}[P]}{\delta P}$ is called the exchange-correlation potential.

The same procedure can be utilized as in the linear case. PET evaluates the modified variational problem by restricting the domain as

$$E^{\mathrm{PET}} = \inf_{\substack{P_s^2 = P_s, P_s^* = P_s \\ P_{0,b}P_s = 0, \mathrm{Tr}P_s = N_s}} \mathcal{E}[P_s + P_{0,b}], \tag{12}$$

which is solved by the following nonlinear eigenvalue problem

$$H[P]|_{\mathcal{B}_0^\perp}\Psi_s = \Psi_s\Lambda_s, \quad P_s = \Psi_s\Psi_s^*, \quad P = P_s + P_{0,b}. \tag{13}$$

Numerical results for real chemical systems, using KSSolve [4], indicate that the PET approach can provide reasonably accurate approximation to the density matrix and the energy, even when the system is relatively small.

References

[1] F. R. Manby, M. Stella, J. D. Goodpaster and T. F. Miller III, *A simple, exact density-functional-theory embedding scheme*, J. Chem. Theory Comput., **8** (2012), pp. 2564–2568.

[2] T. Nguyen, A. A. Kananenka and D. Zgid, *Rigorous Ab Initio Quantum Embedding for Quantum Chemistry Using Green's Function Theory: Screened Interaction, Nonlocal Self-Energy Relaxation, Orbital Basis, and Chemical Accuracy*, J. Chem. Theory Comput., **12** (2016), pp. 4856–4870.

[3] Q. Sun and G. K.-L. Chan, *Quantum embedding theories*, Acc. Chem. Res., **49** (2016), pp. 2705–2712.

[4] C. Yang, J. C. Meza, B. Lee and L. W. Wang, *KSSOLV—a MATLAB toolbox for solving the Kohn-Sham equations*, ACM Trans. Math. Software, **10** (2009), 110.

Cubic scaling algorithm for RPA correlation energy using interpolative separable density fitting

Kyle Thicke
(joint work with Jianfeng Lu)

In Kohn-Sham Density Functional Theory (KS DFT), the ground state energy of a system can be written as

$$E = T_{\mathrm{s}} + U_{\mathrm{ext}} + U_{\mathrm{H}} + E_{\mathrm{xc}}, \tag{1}$$

where T_{s} is the kinetic energy of the non-interacting system, U_{ext} is the energy from the external potential, U_{H} is the Hartree energy, and E_{xc} is the so-called exchange-correlation energy. The first three terms are well known, and given the Kohn-Sham orbitals, it is straightforward to compute them. A simple explicit expression for the exchange-correlation energy is not known, so it is approximated in practice [2]. In this work, we consider the Random Phase Approximation (RPA) for the correlation energy [3].

$$E_{\mathrm{c}}^{\mathrm{RPA}} = \frac{1}{4\pi} \int_{-\infty}^{\infty} \mathrm{tr}\left[\ln(1 - \chi^0(i\omega)v_c) + \chi^0(i\omega)v_c\right] \mathrm{d}\omega, \tag{2}$$

where

$$\chi^0(x, y; i\omega) = \sum_{j}^{\mathrm{occ}} \sum_{k}^{\mathrm{vir}} \frac{\psi_j^*(x)\psi_k(x)\psi_k^*(y)\psi_j(y)}{\epsilon_j - \epsilon_k - i\omega} + \mathrm{c.c.}, \tag{3}$$

v_c is the Coulomb kernel, and $\{\psi_j\}$ are the Kohn-Sham orbitals. We are considering the zero temperature case where the first N_{occ} orbitals are occupied and rest are unoccupied (virtual).

Under this approximation, the bottleneck in the computation is the construction of χ^0, which takes $O(N^4)$ time, where N is a parameter describing the system size. All other steps take only cubic time in N. In order to compute (3) in cubic time, we split up the dependence of j and k in the denominator by using Cauchy's integral formula,

$$\chi^0(x, y; i\omega) = \frac{1}{2\pi i} \int_{\mathcal{C}} \left(\sum_{j}^{\mathrm{occ}} \frac{\psi_j^*(x)\psi_j(y)}{\lambda - \epsilon_j + i\omega} \right) \left(\sum_{k}^{\mathrm{vir}} \frac{\psi_k(x)\psi_k^*(y)}{\lambda - \epsilon_k} \right) \mathrm{d}\lambda + \mathrm{c.c.}, \tag{4}$$

where $\mathcal{C}$ is a negatively oriented curve that encircles all $\{\epsilon_k\}_{k\in\mathrm{vir}}$, but not any $\{\epsilon_j \pm i\omega\}_{j\in\mathrm{occ}}$.

The strategy to obtain (4) has been utilized in [8]. (An alternative strategy, the so-called Laplace transform method, is utilized in [6, 7].) The major contribution of this work is to lower the prefactor in front of the N^3 in the computational cost. Note that if we use (4), then the computation of (2) will still take time proportional to N_{grid}^3, where N_{grid} is the number of grid points. In actual calculations, N_{grid} is typically very large. Therefore, it would be advantageous for us to write the problem into a smaller basis set. We do this using the newly developed interpolative separable density fitting [4, 5].

The traditional density fitting method factors the orbital pair functions as

$$\psi_j^*(x)\psi_k(x) \approx \sum_{\mu=1}^{N_{\text{aux}}} C_{jk}^{\mu} P_\mu(x), \tag{5}$$

where $\{P_\mu\}$ are user-chosen basis functions and the coefficients C_{jk}^{μ} are found by solving least squares problems (which takes $O(N^4)$ time). The interpolative separable density fitting method factors the orbital pair functions as

$$\psi_j^*(x)\psi_k(x) \approx \sum_{\mu=1}^{N_{\text{aux}}} \underbrace{\psi_j^*(x_\mu)\psi_k(x_\mu)}_{\text{coefficient}} P_\mu(x), \tag{6}$$

where $\{P_\mu\}$ are the new basis functions (which are computed by the algorithm) and $\psi_j^*(x_\mu)\psi_k(x_\mu)$ are the coefficients in front of the basis functions. The splitting of the j and k dependence in the coefficient is crucial for the application to our problem. Additionally, computing the factorization only takes $O(N^3)$ time. By writing the problem into this new basis, we reduce the computational complexity of the cubic scaling algorithm from $O(N_{\text{grid}}^3)$ to $O(N_{\text{aux}}^2 N_{\text{grid}})$. This is a significant savings since N_{aux} has been shown empirically to be much smaller than N_{grid} [4, 1].

References

[1] J. Lu and K. Thicke, *Cubic scaling algorithms for RPA correlation using interpolative separable density fitting*, Journal of Computational Physics, **351**, (2017), pp. 187–202.

[2] J. Perdew and K. Schmidt, *Jacob's ladder of density functional approximations for the exchange-correlation energy*, AIP Conference Proceedings, Vol. **577**, No. 1, AIP, 2001.

[3] X. Ren et al., *Random-phase approximation and its applications in computational chemistry and materials science*, Journal of Materials Science, **47** (21), (2012), pp. 7447–7471.

[4] J. Lu and L. Ying, *Compression of the electron repulsion integral tensor in tensor hypercontraction format with cubic scaling cost*, Journal of Computational Physics, **302**, (2015), pp. 329–335.

[5] J. Lu and L. Ying, *Fast algorithm for periodic density fitting for Bloch waves*, Annals of Mathematical Sciences and Applications, **1** (2), (2016), pp. 321–339.

[6] M. Kaltak, J. Klimeš and G. Kresse, *Low scaling algorithms for the random phase approximation: Imaginary time and Laplace transformations*, Journal of Chemical Theory and Computation, **10** (6), (2014), pp. 2498–2507.

[7] M. Kaltak, J. Klimeš and G. Kresse, *Cubic scaling algorithm for the random phase approximation: Self-interstitials and vacancies in Si*, Physical Review B, **90** (5), (2014), 054115.

[8] J. Moussa, *Cubic-scaling algorithm and self-consistent field for the random-phase approximation with second-order screened exchange*, The Journal of Chemical Physics, **140** (1), (2014), 014107.

`molsturm`: Modular electronic structure theory framework

Michael F. Herbst
(joint work with James E. Avery, Guido Kanschat and Andreas Dreuw)

The talk gives an overview of our recent efforts to simplify the investigation of novel types of basis functions for quantum-chemical calculations [1]. Motivated by Coulomb-Sturmians as basis functions for quantum-chemistry simulations the design of the flexible and light-weight quantum-chemical method development framework `molsturm` [2, 3] is outlined, where new discretisation methods for electronic structure theory calculations can be easily implemented and tested.

First a list of desirable properties for a basis in the context of quantum chemistry is reviewed. Amongst other aspects an ideal basis would be able to (1) accurately represent the physics of a chemical system, and (2) allow for systematic improvements aided by error estimates, whilst it (3) gives rise to numerically feasible discretised problems. The predominant basis function type in electronic structure theory, namely contracted Gaussian-type orbitals (cGTO) [4, 5], leads to comparatively simple discretised problems as well as an acceptable accuracy for most applications. These functions do, however, not satisfy the first two aforementioned criteria perfectly. For example, they are not able to properly describe the region of a state where electron and nucleus are close, see figure 1.

Our recent research has looked into so-called Coulomb-Sturmians (CS) as an alternative. These exponentially decaying functions are isoenergetic, analytical solutions to a partial differential equation, which is related to the Schrödinger equation for a single-electron system by scaling the nuclear attraction potential [6, 7]. They form a complete basis for $H^1(\mathbb{R}^3)$ and are able to correctly reproduce the physical features of the wave function, i.e. both the nuclear cusp as well as proper exponential decay [8]. Figure 1 displays the local energy for the hydrogen atom at small electron-proton distances if selected cGTO and CS basis sets are used for the discretisation. For cGTO discretisations the large fluctuations of the local energy at small distances are indicative of deviations of the obtained approximate eigensolution from being a true eigensolution. This is not improved much for distances less than 0.1 Bohr if a larger cc-pV6Z basis is used. In contrast for CS-based discretisations the behaviour is more uniform and the larger $(4, 1, 1)$ basis has local energies closer to -0.5 than $(3, 1, 1)$ over the full depicted range.

Ideally one would not need to restart development from scratch for each new type of basis function, but would be able to utilise already existing quantum-chemistry programs as much as possible. A direct implementation of a new basis function type into an existing quantum chemistry programs is, however, typically challenging, since the numerical properties differ substantially between discretisation methods. To give an illustration, figure 2 shows the sparsity as well as the size of the Fock matrices resulting from different discretisation approaches applied to a Hartree-Fock (HF) self-consistent field (SCF) calculation of beryllium. In some cases, like CS-based discretisations, unusual angular-momentum selection rules

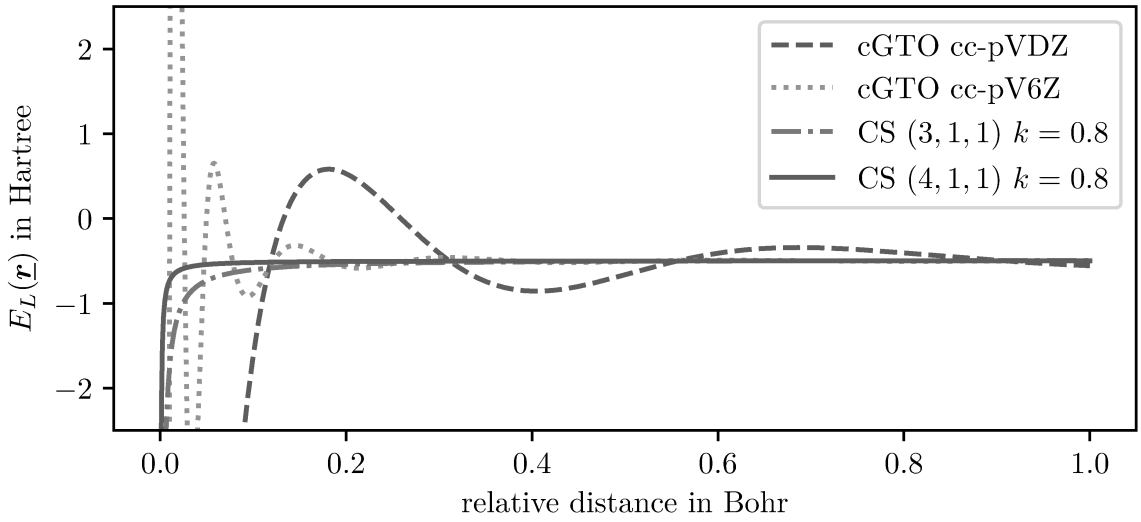


FIGURE 1. Plot of local energy $E_L(\underline{\boldsymbol{r}})$ versus radial distance of electron and proton for the hydrogen atom. Shown is the region where electron and proton are close. The exact local energy is -0.5 and deviations can be understood as the relative error of the discretised solution to being a true eigensolution of the Schrödinger equation [1, 7].

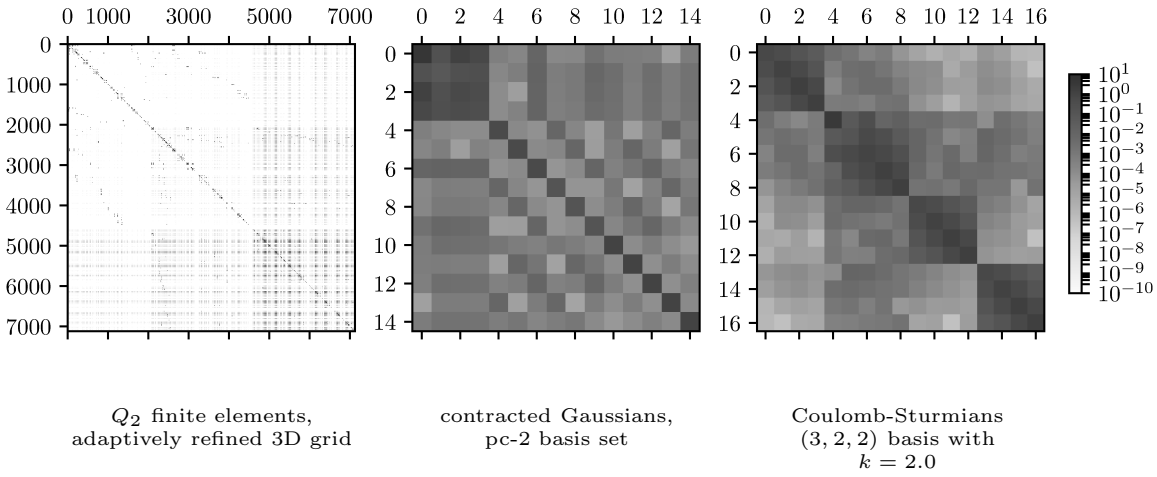


FIGURE 2. Examples of Fock matrices in a Hartree-Fock self-consistent field calculation for beryllium, discretised using finite elements, contracted Gaussians or Coulomb-Sturmians [1, 3].

can reduce computational effort for obtaining the Fock matrix elements further, provided that appropriate evaluation schemes can be used, see [1].

Such deviating numerical demands of different discretisations can be supported by so-called contraction-based methods [1, 3]. In this well-established approach one avoids to store the problem matrices in memory and instead uses matrix-vector

product expressions as the algorithmic basis. Employing a concept called lazy matrices, where all matrix operations are subject to lazy evaluation, `molsturm` [2, 3] features an SCF algorithm, which is completely separated from the code dealing with the discretisation. In `molsturm` it is thus possible to add a new type of discretisation or basis function in a plug and play fashion, i.e. just by implementing the link to the code performing the integral evaluations. Conversely a new algorithm — like an SCF scheme — only needs to be programmed once and immediately can be used with all basis function types available. Thus `molsturm` facilitates employing new mathematical approaches in practice and comparing them on a common setting to the methods already implemented. Lazy matrices are not necessarily limited to the SCF step or the context of quantum chemistry. The library `lazyten` [9] allows them to be used in the context of other physical problems as well.

It is explicitly *not* the goal of `molsturm` to become yet another complete quantum-chemistry package. Much rather the package focuses on solving SCF problems in the most general way possible and handing the results over to third-party packages or other user-provided algorithms building on top. For this reason `molsturm` offers a readily applicable `python` interface, where all relevant quantities can be easily obtained for post-processing. Due to the basis-function-independent nature of the SCF algorithm any novel basis function type implemented in `molsturm` immediately becomes available to algorithms built on top of this framework. Therefore `molsturm` can be thought of as a mediator between low-level developments with respect to novel algorithms and discretisation schemes for solving the HF problem on the one hand and high-level quantum-chemical method development: Both ends are abstracted from each other, but can still benefit from mutual progress.

References

[1] M. F. Herbst, *Development of a modular quantum-chemistry framework for the investigation of novel basis functions*, Ph.D. thesis, Heidelberg University (2018). Dissertation submitted.

[2] M. F. Herbst and J. E. Avery, `https://molsturm.org`, *A modular electronic structure theory code*. Accessed on 10th April 2018.

[3] M. F. Herbst, A. Dreuw and J. E. Avery, *`molsturm`: A light-weight quantum-chemistry framework for rapid method development not restricted to a particular type of basis function.* In preparation.

[4] F. Jensen, *Atomic orbital basis sets*, Wiley Interdisciplinary Reviews: Computational Molecular Science, **3**, 273 (2013).

[5] J. G. Hill, *Gaussian basis sets for molecular applications*, International Journal of Quantum Chemistry, **113**, 21 (2013).

[6] J. Avery and J. Avery, *Generalized Sturmians and Atomic Spectra*, World Scientific (2006).

[7] P. E. Hoggan, *How Exponential Type Orbitals Recently Became a Viable Basis Set Choice in Molecular Electronic Structure Work and When to Use Them*, pp. 199–219, Springer-Verlag, Dordrecht (2009).

[8] J. S. Avery, J. E. Avery, V. Aquilanti and A. Caligiana, *Atomic Densities, Polarizabilities, and Natural Orbitals Derived from Generalized Sturmian Calculations*, Advances in Quantum Chemistry, **47**, 157 (2004).

[9] M. F. Herbst and J. E. Avery, *The lazyten lazy matrix library*, `https://lazyten.org`. Accessed on 10th April 2018.

Reporter: Sören Behr

Participants

Sören Behr
Fakultät für Mathematik
Technische Universität München
Boltzmannstrasse 3
85748 Garching bei München
GERMANY

Prof. Dr. Eric Cancès
CERMICS
Ecole des Ponts and INRIA
Cite Descartes, Champs-sur-Marne
6 et 8 Ave. Blaise Pascal
77455 Marne-la-Vallée Cedex 2
FRANCE

Lingling Cao
CERMICS
Ecole des Ponts and INRIA
Cite Descartes, Champs-sur-Marne
6 et 8 Ave. Blaise Pascal
77455 Marne-la-Vallée Cedex 2
FRANCE

Prof. Dr. Anil Damle
Department of Computer Science
Cornell University
436 Malott Hall
Ithaca, NY 14853-4201
UNITED STATES

Dr. Geneviève Dusson
Mathematics Institute
University of Warwick
Gibbet Hill Road
Coventry CV4 7AL
UNITED KINGDOM

Dr. Virginie Ehrlacher
CERMICS - ENPC
Cite Descartes, Champs-sur-Marne
6 et 8 Avenue Blaise Pascal
77455 Marne-la-Vallée Cedex 2
FRANCE

Fabian M. Faulstich
Department of Chemistry
University of Oslo
Blindern
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Dr. Heinz-Jürgen Flad
Zentrum Mathematik
Technische Universität München
Boltzmannstrasse 3
85748 Garching bei München
GERMANY

Prof. Dr. Gero Friesecke
Fakultät für Mathematik
Technische Universität München
Boltzmannstrasse 3
85748 Garching bei München
GERMANY

Prof. Dr. Jürgen Gauss
Institut für Physikalische Chemie
Johannes-Gutenberg Universität Mainz
Duesbergweg 10-14
55128 Mainz
GERMANY

Prof. Dr. David Gontier
CEREMADE
Université Paris Dauphine
Place du Marechal de Lattre de Tassigny
75775 Paris Cedex 16
FRANCE

Prof. Dr. Trygve Helgaker
Department of Chemistry
University of Oslo
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Dr. Michael F. Herbst
Interdisziplinäres Zentrum für
wissenschaftliches Rechnen
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 205
69120 Heidelberg
GERMANY

Dr. Venera Khoromskaia
Max-Planck-Institut für Mathematik
in den Naturwissenschaften
Inselstrasse 22 - 26
04103 Leipzig
GERMANY

Dr. Boris N. Khoromskij
Max-Planck-Institut für Mathematik
in den Naturwissenschaften
Inselstrasse 22 - 26
04103 Leipzig
GERMANY

Dr. Simen Kvaal
Centre for Theoretical and
Computational Chemistry
University of Oslo
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Dr. Andre Laestadius
Department of Chemistry
University of Oslo
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Prof. Dr. Caroline Lasser
Zentrum Mathematik
Technische Universität München
Boltzmannstrasse 3
85748 Garching bei München
GERMANY

Prof. Dr. Antoine Levitt
Ecole des Ponts ParisTech
Cité Descartes - Champs sur Marne
6 et 8 Avenue Blaise Pascal
77455 Marne-la-Vallée Cedex 2
FRANCE

Prof. Dr. Mathieu Lewin
CEREMADE
Université Paris-Dauphine
Place du Marechal de Lattre de Tassigny
75775 Paris Cedex 16
FRANCE

Prof. Dr. Lin Lin
Department of Mathematics
University of California, Berkeley
1083 Evans Hall
Berkeley CA 94270
UNITED STATES

Michael J. Lindsey
Department of Mathematics
University of California, Berkeley
970 Evans Hall
Berkeley CA 94720-3840
UNITED STATES

Prof. Dr. Christian Lubich
Mathematisches Institut
Universität Tübingen
Auf der Morgenstelle 10
72076 Tübingen
GERMANY

Prof. Dr. Christoph Ortner
Mathematics Institute
University of Warwick
Zeeman Building
Coventry CV4 7AL
UNITED KINGDOM

Prof. Dr. Ivan Oseledets
Skolkovo Institute of Science and Technology
Skolkovo Nobel St. 3
Moscow 143 026
RUSSIAN FEDERATION

Prof. Dr. Gianluca Panati
Dipartimento di Matematica
Universita di Roma "La Sapienza"
Istituto "Guido Castelnuovo"
Piazzale Aldo Moro, 2
00185 Roma
ITALY

Prof. Dr. Thomas Bondo Pedersen
Department of Chemistry
University of Oslo
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Elias Polak
Département de Mathématiques
Université de Geneve
Case Postale 64
2-4, rue du Lievre
1211 Genève 4
SWITZERLAND

Dr. Lucia Reining
Laboratoire des Solides Irradiés
École Polytechnique
91128 Palaiseau cedex
FRANCE

Prof. Dr. Trond Saue
Laboratoire de Chimie et Physique Quantiques
Université Paul Sabatier
118, route de Narbonne
31062 Toulouse Cedex 9
FRANCE

Prof. Dr. Andreas Savin
Laboratoire de Chimie Théorique
CNRS UMR 7616
Université de Pierre et Marie Curie
Case 137, 4 place Jussieu
75252 Paris Cedex 05
FRANCE

Prof. Dr. Reinhold Schneider
Fakultät II - Institut für Mathematik
Technische Universität Berlin
Sekr. MA 5-3
Straße des 17. Juni 136
10623 Berlin
GERMANY

Sami Siraj-Dine
CERMICS
Ecole des Ponts and INRIA
Cite Descartes, Champs-sur-Marne
6 et 8 Ave. Blaise Pascal
77455 Marne-la-Vallée Cedex 2
FRANCE

Prof. Dr. Benjamin Stamm
MATHCCES
Department of Mathematics
RWTH Aachen University
Schinkelstrasse 2
52062 Aachen
GERMANY

Prof. Dr. Andrew Teale
School of Chemistry
University of Nottingham
Room B32
University Park
Nottingham NG7 2RD
UNITED KINGDOM

Dr. Erik Tellgren
Centre for Theoretical and
Computational Chemistry
University of Oslo
Blindern
P.O. Box 1033
0315 Oslo
NORWAY

Kyle Thicke
Department of Mathematics
Duke University
P.O.Box 90320
Durham, NC 27708-0320
UNITED STATES

Prof. Dr. Robert van Leeuwen
Department of Mathematics
University of Jyväskylä
Seminaarinkatu 15
40100 Jyväskylä
FINLAND

Prof. Dr. Chao Yang
Computational Research Division
Lawrence Berkeley National Laboratory
MS-50F
1, Cyclotron Road
Berkeley CA 94720
UNITED STATES

Prof. Dr. Harry Yserentant
Institut für Mathematik
Technische Universität Berlin
Straße des 17. Juni 136
10623 Berlin
GERMANY

Dr. Leonardo Zepeda-Núñez
Department of Mathematics
Lawrence Berkeley National Laboratory
B 50E-1502
Berkeley, CA 94708
UNITED STATES

Prof. Dr. Aihui Zhou
Institute of Computational Mathematics
and Scientific/Engineering Computing
Academy of Mathematics and Systems
Science
Chinese Academy of Sciences
Beijing 100 190
CHINA