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Particle-hole symmetry in many-body theories of electron correlation

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ABSTRACT
Second quantized creation and annihilation operators for fermionic particles anti-commute, but the same is true for the creation and annihilation operators for holes. This introduces a symmetry into the quantum theory of fermions that is absent for bosons. In *ab initio* electronic structure theory it is common to classify methods by the number of electrons for which the method returns exact results: for example Hartree-Fock theory is exact for one-electron systems, whereas coupled-cluster theory with single and double excitations is exact for two-electron systems. Here we discuss the generalization: methods based on approximate wavefunctions that are exact for n-particle systems are also exact for n-hole systems. Novel electron correlation methods that attempt to improve on the coupled-cluster framework sometimes retain this property, and sometimes lose it. Here we argue for retaining particle-hole symmetry as a desirable design criterion of approximate electron correlation methods. Dispensing with it might lead to loss of n-representability of density matrices, and this in turn can lead to spurious long-range behaviour in the correlation energy.

1. Introduction

Since the widespread adoption of coupled-cluster (CC) theory in quantum chemistry [1–3] there have been many attempts to fix its deficiencies by including additional terms, or by leaving certain terms out. The former is perhaps best illustrated by the perturbative (T) correction [4], but also includes attempts to capture low-scaling contributions from variational coupled-cluster theory [5]. Theories that resemble CCSD but lack certain terms are more plentiful, and include linearised CC [1, 6, 7], various coupled electron-pair approximations [8], the nCC hierarchy from the Bartlett group [9], the pCCSD family of methods from the Nooijen group [10, 11], the approximate coupled-pair approaches of Paldus and Piecuch [12–14], and many others. Most recently, this class of methods has been joined by the distinguishable cluster approximation [15].

Deletion of terms from CCSD seems in many cases to improve accuracy, rather than reduce it. Many studies demonstrate that the approximate coupled-pair approach with

approximate quadruples (ACPQ) is superior to the full CCSD method for strongly correlated systems [12–14, 16]. At the same time the accuracy of ACPQ in the weakly correlated regime is similar to that of CCSD [9, 14]. On the other hand, the parameterised CCSD methods (pCCSD), developed as orbital-invariant extensions of CEPA methods, are much more accurate than CCSD for dynamical correlation (particularly the pCCSD(−1, 1) version), but like CCSD are completely unreliable for static correlation [10, 11]. The pCCSD(1, 0) method is closely related to ACPQ (and equal to 2CC [9]) and can be used for strongly correlated systems, albeit at the expense of reduced accuracy for weakly correlated systems [10].

The distinguishable cluster doubles (DCD) approach combines the strengths of the two approaches providing similar (or even higher) accuracy than ACPQ in the strongly correlated regime, and similar accuracy to pCCSD(−1, 1) in the weakly correlated regime [15, 17, 18]. Orbital relaxation in the distinguishable cluster method can be handled in any of the standard ways for coupled-cluster theory, i.e., using Brueckner orbitals, orbital optimization, or single excitations (DCSD) [17].

It is widely recognised that in selecting subsets of diagrams to include in approximate correlation theories, certain design principles should be applied. For example, in most successful theories full diagrammatic expressions are retained, which provides invariance to unitary transformations within the occupied orbitals, or within the virtuals, and extensivity in the ground-state energy. It is also reassuring to ensure exactness for 2-electron systems and thereby, via extensivity, for an arbitrary number of non-interacting 2-electron systems. The CCSD, pCCSD, ACP and DCSD methods all satisfy these three properties of orbital invariance, extensivity and exactness for two-electron systems.

Perhaps there is another exactness property that can guide the construction of approximations, and can help to account for the surprising accuracy of DCSD. Here we will argue that this additional criterion might be particle-hole symmetry.

Wigner's theorem identifies symmetry operations as either being unitary or antiunitary, respectively satisfying

$$\langle \hat{U}\psi | \hat{U}\psi' \rangle = \langle \psi | \psi' \rangle$$
$$\langle \hat{A}\psi | \hat{A}\psi' \rangle = \langle \psi' | \psi \rangle \ ,$$

which either commute or anticommute with the Hamiltonian. The particle-hole operator $\hat{P}$ interchanges particles and holes, and for some Hamiltonians, such as the Bogoliubov-de Gennes Hamiltonian, $\hat{P}$ is an anticommuting antiunitary symmetry.

Here, however, we mean particle-hole symmetry in a different sense: we refer to the natural way in which the roles of particles and holes can be interchanged in fermionic calculations expressed in the language of second quantization. Particle-hole symmetry in this sense was identified by Dirac, who describes [19, p252]

a development of the theory of fermions that has no analogue for bosons. For fermions there are only the two alternatives of a state being occupied or unoccupied and *there is a symmetry between these two alternatives* [Dirac's emphasis].

The creation and annihilation operators for holes are the Hermitian conjugates of
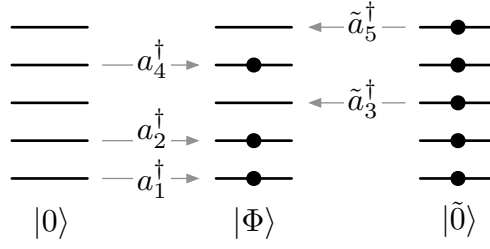
Figure 1. Construction of a particular state $|\Phi\rangle$ by creating particles in the vacuum $(\hat{a}_4^\dagger \hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle)$, or equivalently by creating holes in the hole-vacuum $(\hat{\tilde{a}}_5^\dagger \hat{\tilde{a}}_3^\dagger |\tilde{0}\rangle)$.

the corresponding operators for particles:

$$\hat{\tilde{a}}_p = \hat{a}_p^\dagger \qquad \hat{\tilde{a}}_p^\dagger = \hat{a}_p$$

(here we use tilde to denote quantities related to holes). The adjoint operation preserves the fermionic anticommutation relation

$$[\hat{\tilde{a}}_p, \hat{\tilde{a}}_q^\dagger]_+ = [\hat{a}_p^\dagger, \hat{a}_q]_+ = \delta_{pq} \ ,$$

so the holes are fermions in just the same sense as the particles. Moreover, for a single site the hole number operator $\hat{\tilde{n}} = \hat{\tilde{a}}^\dagger \hat{\tilde{a}}$ has the expected relation to the particle number operator: $\hat{\tilde{n}} = 1 - \hat{n}$.

There is no particular reason to prefer one representation over the other: proper fermionic states can be constructed by applying a string of particle creation operators to the zero-particle vacuum state

$$|\Phi\rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots |0\rangle \ ,$$

or equally well by applying hole creation operators to the hole-vacuum state

$$|\Phi\rangle = \hat{\tilde{a}}_a^\dagger \hat{\tilde{a}}_b^\dagger \cdots |\tilde{0}\rangle \ .$$

Here the hole vacuum $|\tilde{0}\rangle$ is the fully occupied state with one electron in each spin orbital, and a typical situation is illustrated in Figure 1.[1]

As we will show, this basic structure that is built into the quantum mechanics for fermions translates into a symmetry between particles and holes in approximate theories for the many-body problem derived from wavefunctions.

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[1]In quantum chemistry it is common to use a third alternative, the particle-hole formalism, in which determinants are produced by creating pairs of particles and holes in a Fermi vacuum, and we adopt this more conventional formalism below. We use the conventional notation for spin-orbital indices such that $i, j, \ldots$ denote occupied; $a, b, \ldots$ denote virtual; and $p, q, \ldots$ denote arbitrary spin-orbitals.

2. Theory

2.1. Particle-hole symmetry in electronic structure theory

Hartree-Fock theory is an exact theory for one-particle systems: both the Hartree-Fock and the exact wavefunction have the structure $\hat{a}_1^\dagger|0\rangle$ for some suitably constructed $\hat{a}_1^\dagger$. Similarly Hartree-Fock is exact for single-hole systems, i.e. for $n-1$ electrons in n spin-orbitals, because both the Hartree-Fock and exact wavefunctions have the form $\hat{\tilde{a}}_n^\dagger|\tilde{0}\rangle$. Hartree-Fock theory is extensive (setting aside for the moment the size-consistency limitations of the spin-restricted formulation) so it is exact for an arbitrary number of isolated one-particle or one-hole systems, or indeed for a mixture of the two. To give a concrete example, a Hartree-Fock calculation on fluorine (9 electrons) in the STO-3G basis set (5 spatial orbitals, so 10 spin orbitals) is exactly equivalent to full configuration interaction (FCI) in the same basis.

Correlated post-HF methods are often expressed in terms of excited determinants obtained from the HF ground-state determinant through the application of an excitation operator; for example a singly-excited determinant can be constructed as $|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i |\Phi\rangle$. It is clearly the case that each particle excitation operator is equivalent to a corresponding hole de-excitation operator, as in $\hat{a}_a^\dagger \hat{a}_i \equiv \hat{\tilde{a}}_a \hat{\tilde{a}}_i^\dagger$, so that each excited determinant can be constructed either by exciting particles or de-exciting holes. For this reason, a truncated CI expansion such as CISD, which is exact for systems of two particles, is simultaneously exact for systems of two holes; and analogous equivalences exist for all truncated CI methods.

MP2 is exact neither for systems of two particles nor two holes. It is normally thought of as a particle-pair theory — in the sense that the correlation energy is expressed as sum of independent contributions for each electron pair — but it can just as well be viewed as a hole-pair theory, as seen by a simple reordering of summations.

CCSD is exact for two-electron systems and, through the extensivity of the method, for an arbitrary number of isolated two-electron systems. Because each diagram in the CCSD equations is accompanied by the diagram with particle and hole lines interchanged — and this feature is discussed in detail below — it is also exact for two-hole systems. Again extensivity provides that it is exact for any number of non-interacting two-hole systems, and indeed for any system composed of non-interacting fragments that each have either two particles or two holes.

Thus all of the key wavefunction-based methods in quantum chemistry share the property that exactness for some particular model problem defined in terms of particles is reflected in exactness for the analogous model problem in which the role of particles and holes is interchanged.

This is typically not the case for methods that are not derived by substituting a wavefunction ansatz into the Schrödinger equation. For example, in the independent electron pair approximation (IEPA) the correlation energies from separate CI calculations on each electron pair are summed together to give an estimate of the total correlation energy — there is no IEPA wavefunction. The method is obviously exact if there is only a single pair of electrons (or any number of noninteracting pairs), but is not generally exact for systems with a single pair of holes.

2.2. Local particle-hole symmetry in wavefunction methods

As we have seen, formulation of approximate wavefunctions in terms of second-quantized operators leads to a symmetry in the exactness properties of the resulting method. However, derivation of methods in this way leads to an even more restrictive PH symmetry, the *local* PH (LPH) symmetry [20], which can be defined in terms of Goldstone diagrams. A method has LPH symmetry if the interchange of particle and hole in any loop of any diagram in the theory leads to another diagram in the theory (with the same factor). In the following we will demonstrate that LPH symmetry emerges naturally when a theory is formulated in terms of a properly antisymmetric state, and can therefore be viewed as an N-representability requirement for approximate theories.

A convenient way to discuss local particle-hole symmetry in second quantization is by defining all operators in terms of one-electron excitation operators $\hat{\tau}_q^p = \hat{a}_p^\dagger \hat{a}_q$. Many-electron excited determinants can be written as products of these operators acting on the reference determinant

$$|\Phi_{ab\cdots}^{ij\cdots}\rangle = \hat{\tau}_i^a \hat{\tau}_j^b \cdots |\Phi\rangle,$$

and de-excitation operators correspond to the Hermitian conjugate:

$$\hat{\tau}_i^{a\dagger} = \hat{\tau}_a^i. \tag{1}$$

The two-electron part of the Hamiltonian can be written as $\frac{1}{2}(pq|rs)[\hat{\tau}_q^p \hat{\tau}_s^r - \delta_{qr}\hat{\tau}_s^p]$, and contractions of the operators can be realized using the well known commutator relation,

$$[\hat{\tau}_q^p, \hat{\tau}_s^r] = \delta_{qr}\hat{\tau}_s^p - \delta_{ps}\hat{\tau}_q^r. \tag{2}$$

The two terms on the right-hand side of Eq. (2) show the origin of the LPH symmetry: if two one-electron operators are contracted together, two terms arise — one from the contraction of the inner creation and annihilation operators (which usually correspond to virtual orbitals), and one from the outer operators (usually corresponding to the occupied orbitals). Therefore an expression coming from a wavefunction-based formalism can violate the LPH symmetry only if either the excitation operators in the Hamiltonian operator do not run over the complete orbital space, or if the excitation operators in the wavefunction do not correspond to excitations from the occupied to the virtual space, but rather, for example, from the occupied to the occupied space. In the former case, the resulting Hamiltonian can lead to a violation of particle-number conservation, as discussed in sec. 2.3. For example, if we restrict the excitation operator in the Fock operator to act only on occupied space, the corresponding correlated density matrix would have a non-zero trace. In the latter case, the resulting correlated wavefunction becomes contaminated by the reference determinant, since the correlated wavefunction is no longer orthogonal to the reference:

$$\langle \Phi | t_j^i \hat{\tau}_i^j | \Phi \rangle = \sum_i t_i^i.$$

Thus, if a theory can be formulated using second quantization with number-

conserving excitation operators, the resulting equations necessarily possess the LPH symmetry.

2.3. Local particle-hole symmetry and particle number conservation

In this section we will examine how absence of PH or LPH symmetry affects one- and two-electron density matrices. For the sake of clarity we restrict ourselves to the coupled cluster doubles (CCD) theory and its approximations, but these results can be straightforwardly generalized.

2.3.1. Density matrices in diagrammatic approximations

The energy and amplitude equations in standard coupled cluster theory can be obtained by bra-projecting the electronic Schrödinger equation $\hat{H} |CC\rangle = E |CC\rangle$ with an exponentially parametrized wavefunction $|CC\rangle = \exp(\hat{T}) |\Phi\rangle$ using the reference $\langle\Phi|$ or excited determinants $\langle\Phi| \hat{\tau}_\mu^\dagger$, respectively. Here $\hat{H}$ is a normal-ordered Hamiltonian, which can conveniently be partitioned into the effective one-electron Fock operator $\hat{F}$ and the two-electron fluctuation potential $\hat{W}$. In coupled cluster doubles theory, the cluster operator $\hat{T}$ is restricted to double excitations only:

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} T_{ab}^{ij} \hat{\tau}_{ij}^{ab}, \tag{3}$$

where T_{ab}^{ij} are the excitation amplitudes and $\hat{\tau}_{ij}^{ab} = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$ the excitation operators.

The diagrams entering the CCD amplitude equation

$$0 = R_{ab}^{ij} \equiv \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\dagger} \left(\hat{W} + \hat{F}\hat{T}_2 + \hat{W}\hat{T}_2 + \tfrac{1}{2}\hat{W}\hat{T}_2^2 \right)_{\mathrm{C}} \right| \Phi \right\rangle, \tag{4}$$

where the subscript "C" stands for "connected", are PH symmetric. Moreover, as indicated in sect. 2.2) they have LPH symmetry. This means that exchanging the roles of particle and hole in any loop of any diagram in R_{ij}^{ab} produces another diagram (with the correct factor) that appears in R_{ij}^{ab}.

Approximate models, however, do not necessarily have this feature. Many approximate models have been devised by modifying the amplitude equation by direct removal, addition or rescaling of certain diagrams [8–10, 12–15, 21]. For ease of reference, we will denote such a modification of the residual expression as $\mathbb{M}R_{ij}^{ab}$. Such manipulations could lead to a loss of the LPH symmetry, as the latter is not commonly considered an essential constraint. As we demonstrate below, violation of this symmetry can compromise particle-number conservation in density matrices.

In non-variational wavefunction-based theories such as projected coupled cluster there are two distinct ways to define density matrices: (i) via derivatives of the energy Lagrangian [22] or (ii) directly using the wavefunction. The latter approach is very rare even within the coupled cluster model itself [23], and in approximate theories, that lack an explicit form for the wavefunction, the energy derivative remains the only option.

6

Without an external perturbation, the CCD energy Lagrangian reads:

$$L\left(\overline{\mathbf{T}}, \mathbf{T}\right) = \left\langle \Phi \left| \left(\hat{W}\hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle + \overline{\mathbf{T}} \cdot \mathbf{R} \tag{5}$$

where $\overline{\mathbf{T}}$ and $\mathbf{R}$ are the Lagrange-multiplier and residual vectors, respectively. If one adds external one-electron $\epsilon_1 \hat{X}_1$ and two-electron $\epsilon_2 \hat{X}_2$ perturbations with strengths ϵ_1 and ϵ_2, the CCD Lagrangian takes the form:

$$L\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right) = \left\langle \Phi \left| \left(\hat{W}\hat{T}_2 + \epsilon_2 \hat{X}_2 \hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle + \overline{\mathbf{T}} \cdot \left(\mathbf{R} + \mathbf{R}^X\right), \tag{6}$$

with

$$\left(R^X\right)_{ab}^{ij} = \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\,\dagger} \left(\epsilon_2 \hat{X}_2 + \epsilon_1 \hat{X}_1 \hat{T}_2 + \epsilon_2 \hat{X}_2 \hat{T}_2 + \tfrac{1}{2}\epsilon_2 \hat{X}_2 \hat{T}_2^2\right)_{\mathrm{C}} \right| \Phi \right\rangle. \tag{7}$$

A physical property corresponding to the perturbation $\epsilon_1 \hat{X}_1$ or $\epsilon_2 \hat{X}_2$ can be evaluated as the derivative of the Lagrangian in equation (6) with respect to ϵ_1 or ϵ_2, taken at zero perturbation strength:

$$\begin{aligned}
\left. \frac{dL\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right)}{d\epsilon_1} \right|_{\epsilon_1=0} &= \sum_{ijab} \overline{T}_{ab}^{ij} \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\,\dagger} \left(\hat{X}_1 \hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle \\
&\equiv \sum_{pq} {}^1D_{pq} X_{pq}, \tag{8}
\end{aligned}$$

$$\begin{aligned}
\left. \frac{dL\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right)}{d\epsilon_2} \right|_{\epsilon_2=0} &= \left\langle \Phi \left| \left(\hat{X}_2 \hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle \\
&\quad + \sum_{ijab} \overline{T}_{ab}^{ij} \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\,\dagger} \left(\hat{X}_2 \left[1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2\right]\right)_{\mathrm{C}} \right| \Phi \right\rangle \\
&\equiv \sum_{pqrs} {}^2D_{pq,rs} X_{pq,rs}. \tag{9}
\end{aligned}$$

Here X_{pq} and $X_{pq,rs}$ are the integrals of the one-electron and two-electron perturbation operators, respectively. The expressions in equations (8) and (9) serve as the definitions of the density matrices ${}^1D_{pq}$ and ${}^2D_{pq,rs}$. The correlation energy is expressed via these density matrices as

$$E_{\mathrm{corr}} = \sum_{pq} {}^1D_{pq} F_{pq} + \sum_{pqrs} {}^2D_{pq,rs} \left(pq|rs\right), \tag{10}$$

where $(pq|rs)$ is an electron repulsion integral for spin-orbitals in the chemical notation.

In CCD, the diagrams stemming from the matrix elements in equations (8) and (9) are LPH symmetric. In an approximate theory based on modified amplitude equations $\mathbb{M}\mathbf{R}$, this might no longer be the case, as this modification entails an identical modification $\mathbb{M}\mathbf{R}^X$ of the diagrams in the external perturbation part $\mathbf{R}^X$. Indeed, in case of explicit inclusion of a finite perturbation, it will appear either in the one electron part of the Hamiltonian $\hat{F} \leftarrow \hat{F} + \hat{X}_1$ or the two-electron part $\hat{W} \leftarrow \hat{W} + \hat{X}_2$. Therefore,

if $\mathbb{M}$ destroys the LPH or PH symmetry in the residual equations, the density matrix will lack it as well.

2.3.2. Particle-hole symmetry and the one-electron density matrix

We start by analyzing the role of particle-hole symmetry in the one-electron density matrix of CCD, which has diagonal occupied and virtual blocks with the form

$$
\begin{aligned}
{}^{1}D_{ij} &= -\sum_{abk} \overline{T}_{ab}^{kj} T_{ab}^{ki}, \\
{}^{1}D_{ab} &= \sum_{ijc} \overline{T}_{ac}^{ij} T_{bc}^{ij}.
\end{aligned}
\tag{11}
$$

Since orbital relaxation is not included in the Lagrangian of equation (6), the occupied-virtual blocks of the density matrix are zero. The definition in equation (11) explicitly demonstrates the PH symmetry of the CCD density matrix: the trace of a post-HF density matrix should be zero, and this is obviously fulfilled here because $\sum_i {}^{1}D_{ii} = -\sum_a {}^{1}D_{aa}$.

Now consider an approximate theory, where $\mathbb{M}$ affects the Fock-terms $\hat{F}\hat{T}$ of the CCD residual; in particular we are interested in a modification $\mathbb{M}$ that breaks particle-hole symmetry. Such a modification might be one that selectively erases either the hole *or* the particle Fock contractions in the residual, but not both:

$$
\mathbb{M}^{1-\mathrm{p}} R_{ij}^{ab} = \cdots - 0 \times \left[\sum_{k} T_{ab}^{ik} F_{kj} + T_{ab}^{kj} F_{ki} \right] + \left[\sum_{c} F_{bc} T_{ac}^{ik} + F_{ac} T_{cb}^{kj} \right],
\tag{12}
$$

$$
\mathbb{M}^{1-\mathrm{h}} R_{ij}^{ab} = \cdots - \left[\sum_{k} T_{ab}^{ik} F_{kj} + T_{ab}^{kj} F_{ki} \right] + 0 \times \left[\sum_{c} F_{bc} T_{ac}^{ik} + F_{ac} T_{cb}^{kj} \right].
\tag{13}
$$

Application of $\mathbb{M}^{1-\mathrm{p}}$ or $\mathbb{M}^{1-\mathrm{h}}$ to $\mathbf{R}^{X}$ leads to a loss of the PH symmetry in the density matrices:

$$
{}^{1-\mathrm{p}}D_{ab} = \sum_{ijc} \overline{T}_{ac}^{ij} T_{bc}^{ij} \qquad\qquad {}^{1-\mathrm{p}}D_{ij} = 0,
\tag{14}
$$

$$
{}^{1-\mathrm{h}}D_{ij} = -\sum_{abk} \overline{T}_{ab}^{ki} T_{ab}^{kj} \qquad\qquad {}^{1-\mathrm{h}}D_{ab} = 0.
\tag{15}
$$

From equations (14) and (15) is evident that the trace of neither $^{1-\mathrm{p}}\mathbf{D}$ nor $^{1-\mathrm{h}}\mathbf{D}$ is zero, leading to the occurrence of spurious charges in the system.

The violation of particle number conservation not only leads to artefacts in one-electron properties, but also to unphysical features in the correlation energy. Indeed, according to equation (10) the one-electron density matrix directly affects the correlation energy. We investigate this effect using an example of hydrogen fluoride dimer, by computing the correlation contribution to the interaction energy using a PH symmetric method (for simplicity MP2) and the two variants that violate this symmetry given in equations (12) and (13).
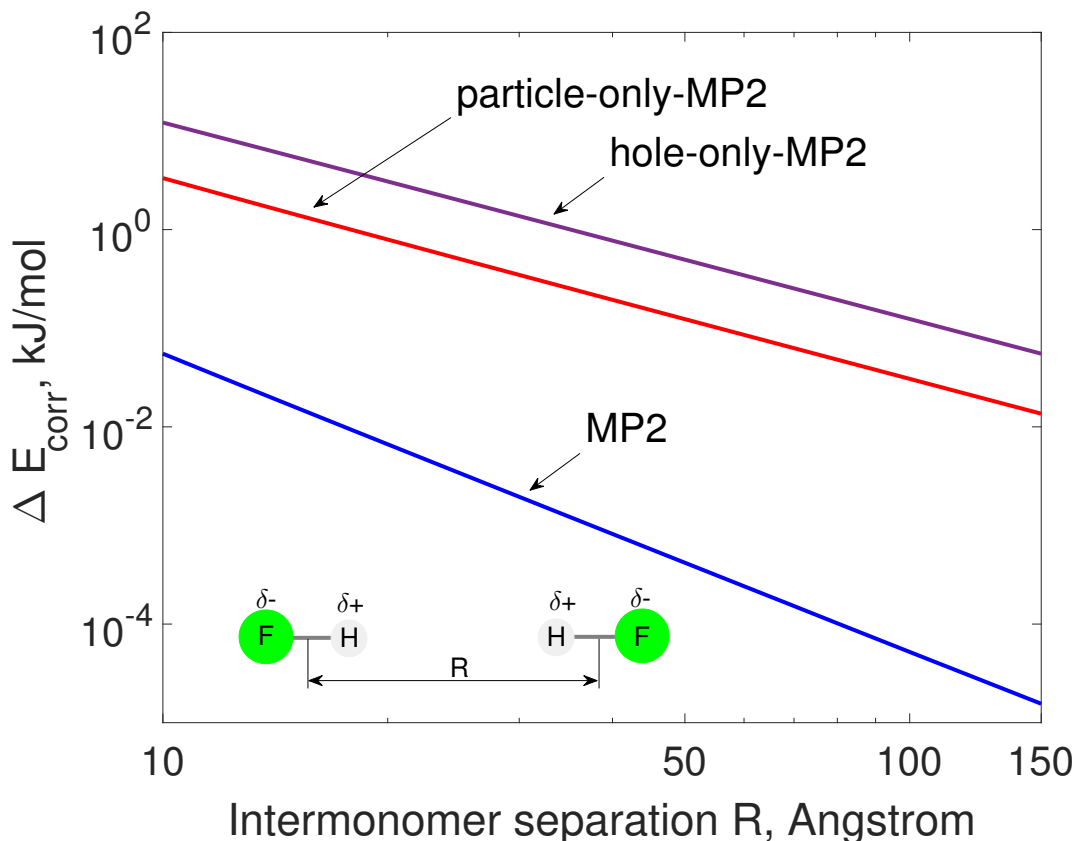
Figure 2. Correlation contribution to the interaction energy for the hydrogen fluoride dimer as a function of the intermonomer separation, computed by MP2, particle-only MP2 and hole-only MP2 methods, and cc-pVDZ basis set. Both axes are scaled logarithmically to linearize the decay rate.

The corresponding potential energy curves (the correlation part thereof) are given in Fig. 2 in the logarithmically scaled axes. According to equation (10) the most slowly decaying component of the interaction energy comes from the electrostatic interaction between the correlated density and the HF density (appearing in the Fock matrix). For MP2 both densities are chargeless (the HF density appearing in the Fock matrix includes the compensating nuclear charges) leading to the R^{-3} decay with intermonomer separation R. However, if the PH symmetry is violated — as it is in equations (12) and (13) — the correlated density matrix acquires spurious charges, leading to an unphysical R^{-2} decay. The erroneous decay properties are clearly visible in Fig. 2.

2.3.3. Local particle-hole symmetry and the two-electron density matrix

To investigate the influence of the LPH symmetry on particle-number conservation in the two-electron density matrix, it is instrumental to consider the "ladder" diagrams[2]

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[2]Conventionally only the first two terms in equation (16) are referred to as ladder diagrams. However, since the four diagrams of equation (16) are interrelated by the LPH symmetry, for convenience we apply the term "ladder diagram" to all of them.

of the CCD residual:

$$R_{ij}^{ab} \quad \leftarrow \quad \sum_{kl} T_{ab}^{kl} (ki|lj) + \sum_{cd} T_{cd}^{ij} (ac|bd)$$
$$- \sum_{kc} T_{cb}^{ik} (ac|kj) - \sum_{kc} T_{ac}^{kj} (ki|bc). \tag{16}$$

The first two terms, as well as the second two terms of equation (16) separately are already PH symmetric. However, the LPH symmetry is guaranteed only if all four terms of equation (16) are taken together.

The ladder diagrams of $\mathbf{R}^X$ involving a two-electron external perturbation can be related to the $^2D_{ik,jl}$, $^2D_{ca,db}$, $^2D_{ab,ij}$ and $^2D_{ij,ab}$ blocks of the two-electron density matrix. The explicit expressions for these contributions $\Delta^2 D$ to the density matrix are:

$$\Delta^2 D_{ik,jl} = \sum_{ab} \overline{T}_{ab}^{kl} T_{ab}^{ij}, \tag{17}$$

$$\Delta^2 D_{ca,db} = \sum_{ij} \overline{T}_{ab}^{ij} T_{cd}^{ij}, \tag{18}$$

$$\Delta^2 D_{ab,ij} = -\sum_{kc} \overline{T}_{ac}^{kj} T_{bc}^{ki}, \tag{19}$$

$$\Delta^2 D_{ij,ab} = -\sum_{ij} \overline{T}_{cb}^{ik} T_{ca}^{jk}. \tag{20}$$

We consider now the partial traces of $\Delta^2 D$ associated with the each of the two electrons:

$$\sum_i \Delta^2 D_{ii,jk} + \sum_a \Delta^2 D_{aa,jk}, \tag{21}$$

$$\sum_i \Delta^2 D_{ii,bc} + \sum_a \Delta^2 D_{aa,bc}, \tag{22}$$

$$\sum_i \Delta^2 D_{jk,ii} + \sum_a \Delta^2 D_{jk,aa}, \tag{23}$$

$$\sum_i \Delta^2 D_{bc,ii} + \sum_a \Delta^2 D_{bc,aa}. \tag{24}$$

In contrast to the "excitonic" terms of the type $\sum_{kc} T_{cb}^{kj} (ki|ac)$, which describe the interaction between an electron and its own hole, the ladders correspond to the interaction between two separate particles or holes. Therefore, particle number conservation demands that all partial traces in equations (21)–(24) are zero, and this is only possible if all four blocks in equations (17)–(20) appear in the two-electron density matrix.

If now in an approximate theory, $\mathbb{M}$ removes some (but not all) ladder diagrams from equation (16), thus eliminating LPH symmetry, some of the DM contributions (21)–(24) will be missing and hence at least some of the traces in equations (17)–(20) will no longer be zero. This will again introduce spurious charges in the two-particle density, causing unphysical artefacts in the two-electron part of the interaction.

To illustrate this effect we have plotted contributions to the MP3 interaction energy $\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$ arising from individual ladder contributions:

$$E_{\text{hh}} = \sum_{ab} \sum_{ijkl} \overline{T}^{ij}_{ab} T^{kl}_{ab} \left(ki|lj\right), \tag{25}$$

$$E_{\text{pp}} = \sum_{abcd} \sum_{ij} \overline{T}^{ij}_{ab} T^{ij}_{cd} \left(ac|bd\right), \tag{26}$$

$$E_{\text{ph}} = -\sum_{abc} \sum_{ijk} \left[\overline{T}^{ij}_{ab} T^{ik}_{cb} \left(ac|kj\right) + \overline{T}^{ij}_{ab} T^{kj}_{ac} \left(ki|bc\right) \right]. \tag{27}$$

The values are shown for an argon dimer as a function of interatomic distance in Fig. 3. Both $\mathbf{T}$ and $\overline{\mathbf{T}}$ are the MP2 amplitudes here, since, due to the symmetry of the Hylleraas functional, the MP2 Lagrange multipliers are identical to the amplitudes.

The decay properties of these terms can be rationalized in the local orbital basis. If the orbitals are localized on the two monomers, corresponding components of the two-electron density matrix asymptotically decay as R^{-6} with intermonomer distance. The Coulomb interaction between the respective densities in accelerates this decay further. If the densities contain spurious charges, the additional factor is only R^{-1} and the overall asymptotic decay is R^{-7}. This is exactly the decay of the individual ΔE_{hh}, ΔE_{pp} and ΔE_{ph} terms seen in Fig. 3. However the physically correct densities are chargeless, which corresponds to at least an R^{-9} decay [24–28]. Indeed, in Fig. 3 the sum of the terms E_{hh}, E_{pp} and E_{ph}, which is LPH symmetric and corresponds to physically correct densities, decays much faster.

As a side note: the rapid decay of the sum of the ladder energy contributions allows for neglect of all four ladder terms for intermolecular pairs in local coupled cluster methods, providing substantial computational savings [25, 26].

3. Conclusion

When electron correlation methods are constructed on the basis of an antisymmetric model wavefunction, symmetries intrinsic in the second quantized operators for fermions are carried over to the resulting method: particle-hole symmetry and local-particle hole symmetry are guaranteed in diagrammatic methods, and typically methods that are exact for a given number of particles are also exact for the same number of holes.

In coupled-cluster methods, density matrices are usually constructed through a response formalism, although this leads to non-n-representable density matrices. Even so, one of the most important requirements of n-representability is satisfied: that the traces of the 1- and 2-particle density matrices are equal to the number of particles or of pairs of particles.

In coupled-cluster-like methods that do not have an explicit form for the wavefunction, there is no option but to compute density matrices in a response formalism. And here the lack of connection to a properly antisymmetrized state can lead to more severe errors in n-representability. As we have seen, when methods are constructed that satisfy LPH symmetry, at least the traces of the 1- and 2-particle density matrices are
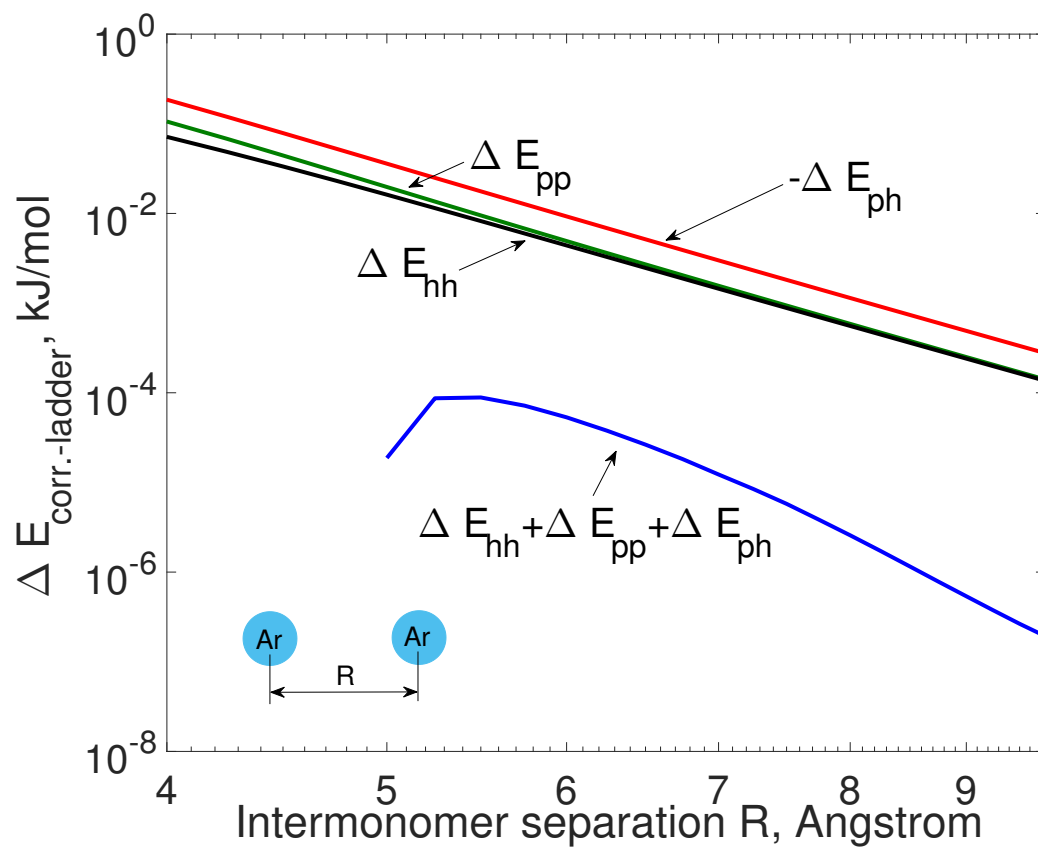
11

Figure 3. The counterpoise corrected ladder-diagram contributions to the MP3 interaction energy for an argon dimer as a function of the interatomic separation. The aug-cc-pVTZ basis set was used. Both axes are scaled logarithmically to linearize the decay rate.

guaranteed to be correct. Violation of this property is not a side issue that arises only for property evaluation, but instead directly impacts on the computation of correlation energies.

It is possible to construct methods that do not satisfy LPH, but do produce density matrices with the correct traces, and pCCSD provides an important example of this type of theory. However it is possible that the lack of LPH symmetry leads to other defects in the theory that are less easily detectable. There is some evidence of this possibility: in the pCCSD(μ, 1) family of methods with $\mu < 0$ the hole-Fock-type mosaic diagram is scaled down (increasingly as μ becomes more negative) while the particle analogue remains unchanged. One interpretation of this is that the screening between particles is not balanced with screening between holes, and one can expect a lowering of the excitation energy as μ is lowered. This agrees perfectly with the findings for EOM-pCCSD: 'as the parameter changes from $\mu = 0$ to -1.5, we find that the excitation energies (for single excited states) decrease fairly systematically' [29]. We will investigate the connection between the the particle-hole symmetry and the conservation of the number of "quasiparticles", that intrinsically include screening effects, in a forthcoming publication.

Finally it is worth noting that when the distinguishable cluster approximation was developed [15, 17, 20], local particle-hole symmetry was used as a design criterion. It may be that the surprising accuracy of the approach arises in part as a consequence of this choice.

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