

University of Groningen

Solution of the Linear-Response Equations in a Basis Set

Boeij, P.L. de

Published in:
Host Publication

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Boeij, P. L. D. (2006). Solution of the Linear-Response Equations in a Basis Set. In *Host Publication* (Lecture Notes in Physics, volume 706; No. 13). Springer.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

13 Solution of the Linear-Response Equations in a Basis Set

P.L. de Boeij

13.1 Introduction

The induced density can be obtained within a linear response calculation by solving a coupled set of equations, in which the first order change in the density $\delta n(\mathbf{r}, \omega)$ follows from the first order change in the self-consistent potential $\delta v_{\text{KS}}(\mathbf{r}, \omega)$ and *vice versa*. Here the induced density can be given as,

$$\delta n(\mathbf{r}, \omega) = \int d^3 r' \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{KS}}(\mathbf{r}', \omega), \quad (13.1)$$

in which the Kohn-Sham response kernel can be expressed in terms of the unperturbed orbital functions $\varphi_i(\mathbf{r})$, orbital energies ε_i , and occupation numbers n_i , using the Lehmann representation,

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,j} (n_j - n_i) \frac{\varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}') \varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i + \omega + i\eta}. \quad (13.2)$$

Here each term is a product of factors that depend only on either \mathbf{r} or \mathbf{r}' . The positive infinitesimal η ensures causality of the response function. The first-order change in the self-consistent potential is given in terms of the induced density by,

$$\delta v_{\text{KS}}(\mathbf{r}, \omega) = \delta v_{\text{ext}}(\mathbf{r}, \omega) + \int d^3 r' \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right\} \delta n(\mathbf{r}', \omega), \quad (13.3)$$

in which we recognize the usual external, Hartree, and exchange-correlation terms. Together with (13.1) and (13.2) this relation completes the self-consistent field scheme for the linear response.

13.2 An Expansion in Orbital Products

By inserting the Lehmann expansion in (13.1), it becomes clear that the factorization of the terms allows to directly integrate the product of the response function and the first order change in the potential. The induced density can then be written as an expansion in terms of orbital products,

$$\delta n(\mathbf{r}, \omega) = \sum_{i,j} \delta P_{ij}(\omega) \varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}), \quad (13.4)$$

in which the expansion coefficients follow from

$$\delta P_{ij}(\omega) = \frac{n_j - n_i}{\varepsilon_j - \varepsilon_i + \omega + i\eta} \int d^3r \varphi_i^*(\mathbf{r}) \delta v_{\text{KS}}(\mathbf{r}, \omega) \varphi_j(\mathbf{r}). \quad (13.5)$$

These coefficients need to be evaluated only for combinations of occupied and virtual orbitals, i.e., for $n_j \neq n_i$, and only for those combinations for which the integrals do not vanish on the basis of symmetry alone. Moreover, we only need to consider positive ω by using the relation $\delta P_{ij}(\omega) = \delta P_{ji}^*(-\omega)$.

The self-consistent field equations can now in principle be solved directly in terms of these expansion coefficients $\delta P_{ij}(\omega)$. Inserting expansion (13.4) for the induced density in the expression for the induced potential (13.3), and using the result to evaluate the integrals in (13.5), this yields a closed expression, given by

$$\begin{aligned} \sum_{k,l} \{(\varepsilon_j - \varepsilon_i + \omega) \delta_{ik} \delta_{jl} - (n_j - n_i) K_{ij,kl}^{\text{Hxc}}(\omega)\} \delta P_{kl}(\omega) \\ = (n_j - n_i) \int d^3r \varphi_i^*(\mathbf{r}) \delta v_{\text{ext}}(\mathbf{r}, \omega) \varphi_j(\mathbf{r}). \end{aligned} \quad (13.6)$$

In this linear set of equations a coupling matrix $K_{ij,kl}^{\text{Hxc}}(\omega)$ enters. It has two contributions being the Hartree term, which is defined as

$$K_{ij,kl}^{\text{H}}(\omega) = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_k^*(\mathbf{r}') \varphi_l(\mathbf{r}'), \quad (13.7)$$

and the exchange-correlation contribution, which is defined as

$$K_{ij,kl}^{\text{xc}}(\omega) = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \varphi_k^*(\mathbf{r}') \varphi_l(\mathbf{r}'). \quad (13.8)$$

13.3 An Efficient Solution Scheme

A first (naïve) estimate for the work needed to solve (13.6) is the amount of elementary operations needed to evaluate all coupling matrix elements, which amounts to a number of floating point operations in the order of $N_{\text{atom}}^6 \bar{n}_{\text{occ}}^2 \bar{n}_{\text{unocc}}^2 \bar{n}_{\text{grid}}^2$. Here N_{atom} is the number of atoms in the system, and \bar{n}_{occ} respectively \bar{n}_{unocc} are the average number of occupied and unoccupied states per atom. \bar{n}_{grid} is the average number of grid points per atom needed to do the integrations. This N_{atom}^6 -scaling becomes prohibitive for larger systems.

Rather than solving the set of linear equations (13.6) directly, a more efficient scheme is possible by using an iterative algorithm [Olsen 1988] like the

conjugate gradient method or the direct inversion of the iterative subspace [Pulay 1980, Pulay 1982] technique. Such methods involve only repeated calculations of the matrix-vector products, which can be performed rather efficiently due to the factorized form of the coupling matrix elements. As initial vector one often chooses to use the uncoupled solution obtained by setting $K^{\text{Hxc}}(\omega) = 0$, i.e.,

$$\delta P_{ij}^{(0)}(\omega) = \frac{n_j - n_i}{\varepsilon_j - \varepsilon_i + \omega + i\eta} \int d^3r \varphi_i^*(\mathbf{r}) \delta v_{\text{ext}}(\mathbf{r}, \omega) \varphi_j(\mathbf{r}). \quad (13.9)$$

In the iteration procedure more accurate vectors are constructed in each cycle, until a converged result is obtained. Usually the number of iterations needed is much smaller than the dimension of the linear set of equations that we want to solve.

The matrix-vector multiplications are best performed in three consecutive steps. As first step the induced density is constructed on a grid of points using the expansion in (13.4). Since the molecular orbitals are often expressed as a linear combination of atom-centered basis functions $\phi_\mu(\mathbf{r})$,

$$\varphi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \phi_{\mu}(\mathbf{r} - \mathbf{R}_{\mu}), \quad (13.10)$$

one can use a similar expansion in terms of the atom-centered functions,

$$\delta n(\mathbf{r}, \omega) = \sum_{\nu, \mu} \phi_{\nu}^*(\mathbf{r} - \mathbf{R}_{\nu}) \phi_{\mu}(\mathbf{r} - \mathbf{R}_{\mu}) \delta \bar{P}_{\mu\nu}(\omega). \quad (13.11)$$

The new coefficients follow from $\delta \bar{P}_{\mu\nu}(\omega) = \sum_{ij} c_{\mu i}^* c_{\nu j} \delta P_{ij}(\omega)$. One can choose to work with the total density, or to break it up into atom-pair densities, and treat each of them in the following steps separately. These atom-pair densities are obtained by grouping the terms in (13.11) per atom pair. These densities are well-localized in space and their expansions contain only few numbers of μ, ν -combinations with non-vanishing overlap, as the atomic functions have exponential tails. This will facilitate the use of distance effects needed to get a linear scaling of the computational cost with increasing system size.

The next step is to evaluate the Coulomb potential for this density. This can be done most efficiently [Baerends 1973] by introducing an auxiliary set of (atom-centered) functions, $f_{\lambda}(\mathbf{r})$, for which the Coulomb integrals can be evaluated analytically,

$$f_{\lambda}^{\text{C}}(\mathbf{r}) = \int d^3r' \frac{f_{\lambda}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (13.12)$$

By fitting the density using these functions, i.e., by expressing the density as $\delta n(\mathbf{r}, \omega) \approx \sum_{\lambda} \bar{c}_{\lambda} f_{\lambda}(\mathbf{r} - \mathbf{R}_{\lambda})$ where the coefficients can be obtained by minimizing the total fit error, one gets

$$\delta v_{\text{H}}(\mathbf{r}, \omega) = \sum_{\lambda} \bar{c}_{\lambda} f_{\lambda}^{\text{C}}(\mathbf{r} - \mathbf{R}_{\lambda}) . \quad (13.13)$$

In order not to introduce spurious long-range terms, it is important to use a constrained fit, in which the charge of the fitted density is exactly reproduced in the fit. If the orbital functions are expressed on a basis of Gaussian-type functions, additional fit functions are not needed, as the atom-pair density can be expressed exactly in terms of Gaussian functions, for which the potentials are known analytically.

The exchange correlation contribution to the potential can now also be evaluated. For the simplest adiabatic local density approximation, for instance, we get,

$$\begin{aligned} \delta v_{\text{xc}}(\mathbf{r}, \omega) &= \int d^3 r' f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', \omega) \delta n(\mathbf{r}', \omega) \\ &= \left. \frac{d^2(e_{\text{xc}}(n))}{dn^2} \right|_{n_{\text{GS}}(\mathbf{r})} \delta n(\mathbf{r}, \omega) , \end{aligned} \quad (13.14)$$

in which $e_{\text{xc}}(n)$ is the exchange-correlation energy density of the homogeneous electron gas.

The third and final step is the evaluation of the matrix elements of the induced potential,

$$\begin{aligned} \sum_{k,l} K_{ij,kl}^{\text{Hxc}}(\omega) \delta P_{kl}(\omega) &= \int d^3 r \varphi_i^*(\mathbf{r}) \delta v_{\text{Hxc}}(\mathbf{r}, \omega) \varphi_j(\mathbf{r}) \\ &= \sum_{\mu,\nu} c_{\mu i}^* c_{\nu j} \int d^3 r \phi_{\mu}^*(\mathbf{r} - \mathbf{R}_{\mu}) \delta v_{\text{Hxc}}(\mathbf{r}, \omega) \phi_{\nu}(\mathbf{r} - \mathbf{R}_{\nu}) . \end{aligned} \quad (13.15)$$

Here too, distance effects can be used by introducing the expansion of the orbitals in terms of atom-centered basis functions.

Each of the steps above involves at maximum in the order of $N_{\text{atom}}^3 \bar{n}_{\text{occ}} \bar{n}_{\text{unocc}} \bar{n}_{\text{grid}}$ floating point operations in case one chooses to work with the total induced density. If instead one uses the atom-pair approach, this factor can be modified to $N_{\text{atom}} \bar{n}_{\text{pairs}} \bar{n}_{\text{bas}}^2 \bar{n}_{\text{grid}}$ for the evaluation of the density and the matrix elements, and to $N_{\text{atom}}^2 \bar{n}_{\text{fit}} \bar{n}_{\text{grid}}$ for the potential. Here the construction of the potential is one order in N_{atom} more expensive as the potential functions $f_{\lambda}^{\text{C}}(\mathbf{r})$ decay only slowly, and need to be evaluated at all grid points in the system. By expressing the long tails in a multipole expansion this unfavorable scaling can be cured [Greengard 1987, White 1994]. Here \bar{n}_{pairs} is the average number of pairs that have overlapping basis functions, \bar{n}_{bas} and \bar{n}_{fit} are the average number of basis and fit functions per atom, and \bar{n}_{grid} is the average number of grid points needed per atom(-pair). Although the atom-pair approach will become more favorable for larger systems, the total density approach can fully utilize the symmetry. Not only can whole blocks of matrix elements be known in advance to vanish due to symmetry,

the grid needed to integrate the remaining terms can also be reduced to cover the irreducible wedge only. In the atom-pair approach symmetry can in general only be used to identify equivalent integrals. A careful analysis of the prefactors involved is needed to determine which approach is more favorable. This will depend on many technical details of the implementation and on the size and symmetry of the system under study.