

Iterative approach for the moment representation of the density-density response function^{*}

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Abstract. The linear density-density response function $\chi(\mathbf{r}, \mathbf{r}')$ can be transformed from its Eigensystem representation into a computationally more efficient moment expansion representation using a suitable unitary transformation. Here, we propose an iterative approach for the direct calculation of this moment representation without resorting to either the direct-space or the conventional Eigensystem representation.

1 Introduction

When atoms and molecules are exposed to various perturbations from the environment, e.g. electric fields from surrounding molecules, they react to this external perturbation with a response of their electronic quantum state. For many small perturbations, perturbation theory can be applied to determine the linear response to the perturbation. This linearity also applies to the electron density in density functional theory (DFT) [1–3], giving rise to density functional perturbation theory (DFPT) [4–9]. The central quantity within linear response theory is the linear density-density response function χ , which connects the (arbitrary) perturbing potential to the induced electronic response density:

$$n_{\text{resp}}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') V_{\text{pert}}(\mathbf{r}') d^3 r', \quad (1)$$

where $n_{\text{resp}}(\mathbf{r})$ denotes the response density and $V_{\text{pert}}(\mathbf{r}')$ denotes the perturbing potential. One possible representation of $\chi(\mathbf{r}, \mathbf{r}')$ is its spectral decomposition in eigenvectors $\chi_i(\mathbf{r})$ and eigenvalues λ_i [10]:

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_i \chi_i(\mathbf{r}) \lambda_i \chi_i(\mathbf{r}') \quad (2)$$

The spectral decomposition can be obtained numerically by a Lanczos diagonalisation technique [10–15].

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The sum in equation (2) can be expressed in the form of a matrix product according to

$$\chi(\mathbf{r}, \mathbf{r}') = \underline{Q} \underline{A} \underline{Q}^T \quad (3)$$

with a vector of functions $\underline{Q} = [\chi_1(\mathbf{r}), \chi_2(\mathbf{r}), \dots]$ and a diagonal real matrix $\underline{A} = [\lambda_1, \lambda_2, \dots]$.

Although the sum in equation (2) is in principle infinite, the spectrum decays, so that it can be truncated after a sufficient number of states. Nevertheless, several thousand states are necessary in order to obtain a converged response density even for small molecules, as we and others have reported [10–16]. This large number of eigenstates presents two problems: it makes, firstly, the computation of the eigenstates very demanding and, secondly, the evaluation of equation (1) rather cumbersome. The latter problem can be solved by a change of representation of the linear density-density response function, generating new states that allow to separate the contributions from different multipole moments of the perturbing potential to the response density. As a consequence, the physical information of the linear density-density response function is condensed in few states [16]. This moment expanded representation provides also a means to solve the former problem, which shall be shown in this paper. A condensed, computationally efficient representation of the density-density susceptibility tensor is crucial for potential applications of intermolecular interactions in the form of polarizable force fields [17–22], but could be of equal interest for the calculation of intermolecular dispersion energies [23–25]. Complementary relevance stems from the area of sum-frequency spectroscopy [26–32], and recently also from “alchemical” morphing between elements [33,34].

The change of representation is achieved by a unitary transformation of the eigenstates that yields irreducible representations of the linear density-density response

function with respect to rotations in $SO(3)$. In the following, we first give a brief summary of the moment expanded representation of the linear density-density response function and show afterwards how this representation drastically reduces the computational effort necessary for the calculation of the response function.

2 Moment expansion

The central idea of the transformation of the density density response function into its moment expansion is that it is possible to determine a unitary transformation for the spectral decomposition of the response function (“Eigensystem representation”) which yields a representation that condenses its physical information in only a few states [16].

In the first step, we expand the perturbing potential in a Laplace series using solid harmonic functions [35]. While other choices such as non-polynomial radial functions (Gaussian, exponential, ...) or a direct cartesian Taylor expansion) are equally possible, we have found solid harmonics to be the most suitable option thanks to their mathematical properties, in particular the existence of a fast and stable method for rotating them in space [35] and the fact that their multipole moments are traceless.

$$V_{\text{pert}}(\mathbf{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^l V_l^m R_l^m(\mathbf{r}'), \quad (4)$$

where

$$V_l^m = \langle V_{\text{pert}} | R_l^m \rangle. \quad (5)$$

Insertion of equations (2) and (4) in (1) yields:

$$n_{\text{resp}}(\mathbf{r}) = \sum_{i=1}^{\infty} \chi_i(\mathbf{r}) \left(\sqrt{\lambda_i} \sum_{l=1}^{\infty} \sum_{m=-l}^l V_l^m \Theta_i^{lm} \right), \quad (6)$$

where we have defined multipole moments

$$\Theta_i^{lm} = \sqrt{\lambda_i} \langle \chi_i | R_l^m \rangle. \quad (7)$$

In the next step, we introduce a new representation of $\chi(\mathbf{r}, \mathbf{r}')$ by a unitary transformation of the eigenstates in equation (3):

$$\chi(\mathbf{r}, \mathbf{r}') = \underline{Q} \underline{\Lambda}^{\frac{1}{2}} \underline{U} \underline{U}^T \underline{\Lambda}^{\frac{1}{2}} \underline{Q}^T =: \underline{R} \underline{R}^T \quad (8)$$

where $\underline{R} = [(\xi_1(\mathbf{r}), \xi_2(\mathbf{r}), \dots)]$ with transformed states

$$\xi_i(\mathbf{r}) := \sum_j^{\infty} U_{ji} \sqrt{\lambda_j} \chi_j(\mathbf{r}). \quad (9)$$

The elements of the transformation matrix \underline{U} are yet to be determined. The aim of this step is to obtain a new set of states $\{\xi_i(\mathbf{r})\}$ which exhibit symmetries of angular momenta with adequate quantum numbers (l, m) . As we

have shown previously [16], it is possible to assign a suitable couple $i \mapsto (l, m)$ to each $\xi_i(\mathbf{r})$ so that a new set of functions $\{\xi_l^m(\mathbf{r})\}$ emerges which satisfies

$$\Xi_{ll'}^{mm'} := \langle \xi_l^m | R_{l'}^{m'} \rangle = 0 \quad \text{if } l > l' \text{ or } m > m'. \quad (10)$$

This property means that a given $\{\xi_l^m(\mathbf{r})\}$ has only contributions from solid harmonics with quantum numbers *larger than* its own ones (l, m) . The new representation of $\chi(\mathbf{r}, \mathbf{r}')$ in terms of the $\xi_l^m(\mathbf{r})$, analogous to equation (2), follows from equation (8):

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_l^{\infty} \sum_{m=-l}^l \xi_l^m(\mathbf{r}) \xi_l^m(\mathbf{r}'). \quad (11)$$

Insertion of this new representation for $\chi(\mathbf{r}, \mathbf{r}')$ into equation (1) and using the Laplace expansion of V_{pert} according to equation (4) yields the response density

$$n_{\text{resp}}(\mathbf{r}) = \sum_{l'=1}^{\infty} \sum_{l=1}^{l'} \sum_{m'=-l'}^{l'} \sum_{m=-l}^l \xi_l^m(\mathbf{r}) \Xi_{ll'}^{mm'} V_{l'}^{m'}, \quad (12)$$

where $\Xi_{ll'}^{mm'}$ from equation (10) has been substituted. The condition expressed in equation (10) has been exploited to reduce the summation limits for l in equation (12) from $(1 \rightarrow \infty)$ to $(1 \rightarrow l')$. Hence, the algorithmic efficiency of the representation of (12) compared to the original one (combining Eqs. (1) and (2)) now depends on a different criterium: it does no more depend on the convergence of the susceptibility spectrum, i.e. the decay of its eigenvalue series (λ_i) , but instead on the quantum number l'_{max} necessary to expand the perturbing potential in terms of solid harmonics functions.

Physically, the coefficients V_l^m represent the (l, m) -components of an external potential expanded at the position of the perturbed molecule/fragment, which is generally several Ångstroms away from the position of the perturbing object. Hence, the spatial variation of $V_{\text{pert}}(\mathbf{r})$ at this distance is likely to be weaker, and the angular moment expansion might be truncated at moderate values of (l, m) :

$$n_{\text{resp}}(\mathbf{r}) = \sum_{l'=1}^{l'_{\text{max}}} \sum_{l=1}^{l'} \sum_{m'=-l'}^{l'} \sum_{m=-l}^l \xi_l^m(\mathbf{r}) \Xi_{ll'}^{mm'} V_{l'}^{m'}. \quad (13)$$

We have demonstrated this for the hydrogen bond interaction in a water dimer[16]: it turns out that $l'_{\text{max}} = 4$ delivers an accurate response density of one water molecule to the perturbing potential of the other one.

The spatial shape of these moment expanded states $\xi_l^m(\mathbf{r})$ for water are discussed in detail in [16] as well. The number of moment expanded states for a maximal angular momentum channel l'_{max} grows with $\mathcal{O}(l'_{\text{max}}^2)$. Thus, a converged response density can be obtained by a number of moment expanded states which is very small compared to the several thousand states of the spectral decomposition.

The algorithm for *obtaining* them according to (8), however, still requires the initial determination of virtually the full spectrum of $\hat{\chi}$, i.e. several thousands of couples $(\lambda_i, \chi_i(\mathbf{r}))$, plus the unitary transformation matrix U_{ij} . In the following section, we will derive an algorithm which allows to compute the moment expanded states directly.

3 Computation of the $\xi_l^m(\mathbf{r})$

In this section, we will present an algorithm which allows to compute the moment expanded states $\xi_l^m(\mathbf{r})$ iteratively, without the need to obtain the spectral decomposition beforehand. In the first step, we determine the response density to a perturbing potential which is equal to the first solid harmonic, i.e.

$$V_{\text{pert}}(\mathbf{r}') = R_1^{-1}(\mathbf{r}'). \quad (14)$$

This is equivalent to setting $V_1^{-1} = 1$ in the Laplace expansion and all other coefficients $V_{l \neq 1}^{m \neq -1} = 0$.

The response density to such a potential is given by equation (13):

$$n_{\text{resp}}(\mathbf{r}) = \sum_{m=-l}^l \xi_l^m(\mathbf{r}) \Xi_{11}^{m-1} \quad (15)$$

$$= n_1^{-1}(\mathbf{r}) = \xi_1^{-1}(\mathbf{r}) \Xi_{11}^{-1-1}. \quad (16)$$

Projection on the solid harmonic $R_1^{-1}(\mathbf{r}')$ yields

$$\langle R_1^{-1} | n_1^{-1} \rangle = |\Xi_{11}^{-1-1}|^2. \quad (17)$$

Eventually, the first moment expanded state $\xi_1^{-1}(\mathbf{r})$ can be obtained by

$$\xi_1^{-1}(\mathbf{r}) = \frac{n_1^{-1}(\mathbf{r})}{\sqrt{\langle R_1^{-1} | n_1^{-1} \rangle}}. \quad (18)$$

The response density to the perturbing potential (14) can be calculated directly by means of an explicit DFPT run, yielding $\xi_1^{-1}(\mathbf{r})$ by equation (18). In order to obtain the state of next higher symmetry $\xi_1^0(\mathbf{r})$, the response density to a perturbing potential equal to the second solid harmonic has to be determined:

$$V_{\text{pert}}(\mathbf{r}') = \xi_1^0(\mathbf{r}'). \quad (19)$$

The response density is then given by equation (13) as

$$n_{\text{resp}}(\mathbf{r}) = \xi_1^{-1}(\mathbf{r}) \Xi_{11}^{-10} + \xi_1^0(\mathbf{r}) \Xi_{11}^{00}, \quad (20)$$

so that follows

$$\begin{aligned} \xi_1^0(\mathbf{r}) \Xi_{11}^{00} &= n_{\text{resp}}(\mathbf{r}) - \xi_1^{-1}(\mathbf{r}) \Xi_{11}^{-10} \\ &=: n_1^0(\mathbf{r}). \end{aligned} \quad (21)$$

Ξ_{11}^{00} can be obtained analogous to equation (17), eventually leading to

$$\xi_1^0(\mathbf{r}) = \frac{n_1^0(\mathbf{r})}{\sqrt{\langle R_1^0 | n_1^0 \rangle}}. \quad (22)$$

The total response density to a perturbing potential

$$V_{\text{pert}}(\mathbf{r}') = R_1^1(\mathbf{r}') \quad (23)$$

is given as:

$$n_{\text{resp}}(\mathbf{r}) = \xi_1^{-1}(\mathbf{r}) \Xi_{11}^{-11} + \xi_1^0(\mathbf{r}) \Xi_{11}^{01} + \xi_1^1(\mathbf{r}) \Xi_{11}^{11}. \quad (24)$$

It follows

$$\xi_1^1(\mathbf{r}) \Xi_{11}^{11} = n_{\text{resp}}(\mathbf{r}) - \xi_1^{-1}(\mathbf{r}) \Xi_{11}^{-11} - \xi_1^0(\mathbf{r}) \Xi_{11}^{01} =: n_1^1(\mathbf{r}) \quad (25)$$

and

$$\xi_1^1(\mathbf{r}) = \frac{n_1^1(\mathbf{r})}{\sqrt{\langle R_1^1 | n_1^1 \rangle}}. \quad (26)$$

The above algorithm can be generalized for the calculation of any moment expanded state $\xi_l^m(\mathbf{r})$ with **specific** (l, m) , which shall be shown in the following. The total response density to a perturbation potential equal to the solid harmonic $R_l^m(\mathbf{r}')$ is

$$n_{\text{resp}}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') R_l^m(\mathbf{r}') d^3 r'. \quad (27)$$

It follows from equations (10) and (13) that

$$n_{\text{resp}}(\mathbf{r}) = \sum_{l'=1}^{l-1} \sum_{m'=-l'}^{l'} \xi_{l'}^{m'}(\mathbf{r}) \Xi_{l'l}^{m'm} + \sum_{m'=-l}^m \xi_l^{m'}(\mathbf{r}) \Xi_{ll}^{m'm}. \quad (28)$$

Furthermore, it follows

$$\begin{aligned} \xi_l^m(\mathbf{r}) \Xi_{ll}^{mm} &= n_{\text{resp}}(\mathbf{r}) - \sum_{l'=1}^{l-1} \sum_{m'=-l'}^{l'} \xi_{l'}^{m'}(\mathbf{r}) \Xi_{l'l}^{m'm} \\ &\quad - \sum_{m'=-l}^{m-1} \xi_l^{m'}(\mathbf{r}) \Xi_{ll}^{m'm} =: n_l^m(\mathbf{r}). \end{aligned} \quad (29)$$

If all the moment expanded states of lower symmetry (l', m') are known, $\xi_l^m(\mathbf{r})$ can be easily calculated:

$$\xi_l^m(\mathbf{r}) = \frac{n_l^m(\mathbf{r})}{\sqrt{\langle R_l^m | n_l^m \rangle}}. \quad (30)$$

Since the explicit calculation of a single state using DFPT requires only one additional perturbation calculation, only $l^2 + l + m$ perturbation calculations are necessary to compute a moment expanded state of order (l, m) . This drastically reduces the computational effort and the required storage in comparison to the computation of several thousand eigenstates for the spectral decomposition

according to equation (2). In the case of a water dimer, the corresponding numbers are about 5000 DFPT iterations (one for each Lanczos step) and 3000 retained Eigenfunctions $\chi_i(\mathbf{r})$ for the original scheme using equation (2), compared to 25 DFPT calculations for all new states up to $l_{\max} = 4$ and the same number of 25 retained functions $\xi_l^m(\mathbf{r})$.

4 Conclusion

We have derived an iterative method for the efficient and direct computation of the linear density-density response function in its moment expanded representation. Our novel method does not rely on the convergence of the Lanczos-based diagonalisation of the response tensor $\chi(\mathbf{r}, \mathbf{r}')$ and the determination of the subsequent transformation of the spectral decomposition into the moment expanded states. Instead, the moment expanded states $\xi_l^m(\mathbf{r})$ are obtained directly from the elementary iterations of the response function.

The moment expanded representation of the density-density response function allows new insight into the nature of the reaction of a complex set of molecular orbitals to external perturbations such as intermolecular interactions.

The considerable increase in algorithmic efficiency relies on the possibility to expand the perturbing potential in a comparably small number of solid harmonics functions, i.e. to truncate the sum in equation (4) at low values of l . While in principle, this truncation does *not* depend on the size of the molecule (rather on the spatial variation of the perturbing potential), it is clear that for a large molecule, this variation will most likely be larger. Hence, the algorithmic advantage of our new scheme may somewhat shrink. However, for a large molecule, the decay of the regular Eigenvalue spectrum of the susceptibility tensor will be much slower than for a small molecule. Hence, the new scheme will again be more advantageous compared to the direct Eigensystem representation according to equation (2).

It should be noted that neither the increase in efficiency nor the accuracy do *not* rely on the properties (size, molecular symmetry, ...) of the molecule under consideration, but instead on the variability of the external potential in the region of that molecule. In turn, this means that for an external potential that has a very anisotropic shape in the region of the considered molecule, the expansion of the potential in terms of solid harmonics may be difficult to converge and the response calculation via equation (13) may become inaccurate for small values of l_{\max} . We believe that many common intermolecular interaction types such as hydrogen bonds and polarization effects due to polar and ionic groups can be represented with a very modest quantum number of about $l_{\max} = 4$.

Author contribution statement

A. Scherrer developed the idea of using symmetry-adapted starting functions for the iterative response calculation scheme and implemented the code; P. Ahlert

and C. Dressler were responsible for benchmarking and application calculations; D. Sebastiani initiated and supervised the project. All authors were involved in the preparation of the manuscript and have approved its final version.

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