Theoretical Spectroscopy for Finite Systems

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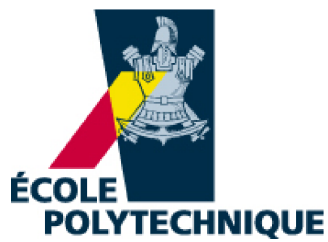

Introduction

This work deals with the calculation of linear-response properties of finite systems using time-dependent density-functional theory (TDDFT) as well as many-body perturbation theory, namely the Bethe-Salpeter equation (BSE). We are especially interested in the performance of these methods when applied to large finite systems (e.g. biological systems). The existing theory used for extended systems needs to be reformulated in order to make these calculations for finite systems feasible. In this work we will in particular focus on an efficient evaluation of the independent-particle density-density response function.

The standard approach to calculate the response function is by doing a sum over states. In practice this sum has to be truncated. However to reach convergence one typically needs to include a number of unoccupied states equal to the number of occupied states. For large systems this can become very costly. We will show that this can be reformulated such that we are left with a summation over occupied states only.

Theoretical Spectroscopy

We are interested in the linear response of finite or lattice periodic systems due to an applied external field. In particular we are interested in obtaining the inverse dielectric function $\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ (GW) and the polarizability $\alpha(\mathbf{r})$ as well as their macroscopic averages. In general they are tensors. However, in the case of a longitudinal external field they become scalars for cubic systems in the long-wavelength limit. They are related to the density-density response function. In the linear response regime these relations are given by

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}'' \frac{\chi_{nn}(\mathbf{r}'', \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}''|}$$

$$\alpha(\mathbf{r}, \omega) = \int d\mathbf{r}' \mathbf{r} \chi_{nn}(\mathbf{r}, \mathbf{r}', \omega) \mathbf{r}'$$

If the response function describes the change of the density due to the change of the external potential in a system that consists of independent particles then this independent-particle response function $\chi^0_{nn}(\mathbf{r}, \mathbf{r}', \omega)$ is given by

$$\chi^0_{nn}(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \to 0^+} \sum_{i,j} (f_i - f_j) \frac{\phi^*_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi^*_j(\mathbf{r}') \phi_i(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

where the wavefunctions ϕ, the energies ϵ and the occupation numbers f are all properties of the ground state.

The Response Function from TDDFT

From Kohn-Sham theory we know that (under some conditions) there exists a unique external potential $v_s(\mathbf{r}, t)$ that generates a time-dependent density $n(\mathbf{r}, t)$ in a noninteracting system that is identical to the time-dependent density in the interacting system with an external potential $v(\mathbf{r}, t)$. The Kohn-Sham response function $\chi_s(\mathbf{r}t, \mathbf{r}'t')$ is the functional derivative of the density with respect to $v_s(\mathbf{r}, t)$. It is simply given by the expression for the independent-particle response function in which the wavefunctions are the ground-state Kohn-Sham wavefunctions. The density-density response function can be obtained from the Kohn-Sham response function by solving

$$\chi_{nn}(1,2) = \chi_{s,nn}(1,2) + \int d3d4\chi_{s,nn}(1,3)[w(3,4) + f_{xc}(3,4)]\chi_{nn}(4,2)$$

where we used the notation $1 = \mathbf{r}_1, t_1$ The exchange-correlation kernel f_{xc} is defined as

$$f_{xc}(1,2) = \frac{\delta v_{xc}(1)}{\delta \rho(2)}$$

where v_{xc} is defined by

$$v_s(1) = v(1) + v_H(1) + v_{xc}(1)$$

with v_H the Hartree potential:

$$v_H(1) = \int d2\rho(2)w(1,2) \qquad w(1,2) = \delta(t_1 - t_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$$

The Response Function from the Bethe-Salpeter Equation

The Bethe-Salpeter equation (BSE) is given by

$$\begin{aligned} L(1,2,3,4) &= L_0(1,2,3,4) + \int d5d6d7d8 L_0(1,2,5,6)K(5,6,7,8)L(7,8,3,4) \\ K(1,2,3,4) &= \delta(1,2)\delta(3,4)w(1,3) + i\frac{\delta\Sigma(1,2)}{\delta G(3,4)} \end{aligned}$$

Here $L(1,2,3,4)$ is the 4-point polarizability, it is related to the two-particle Green function G_2 according to

$$\begin{aligned} L(1,2,3,4) &= L^0(1,4,3,2) - G_2(1,2,3,4) \\ L^0(1,2,3,4) &= iG(1,3)G(4,2) \end{aligned}$$

Its relation to χ_{nn} is simply given by $\chi_{nn}(1,2) = L(1,1,2,2)$. We can express the BSE in a basis according to

$$L_{(n_1 n_2)(n_3 n_4)} = L^0_{(n_1 n_2)(n_3 n_4)} + L^0_{(n_1 n_2)(n_5 n_6)} K_{(n_5 n_6)(n_7 n_8)} L_{(n_7 n_8)(n_3 n_4)}$$

$$L_{(n_1 n_2)(n_3 n_4)} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 L(1,2,3,4)\phi_{n_1}(\mathbf{r}_1)\phi^*_{n_2}(\mathbf{r}_2)\phi^*_{n_3}(\mathbf{r}_3)\phi_{n_4}(\mathbf{r}_4)$$

The $\{\phi_i\}$ can be any complete basis. We can use for example the Kohn-Sham wavefunctions. They render L^0 diagonal since they are an orthogonal basis. The subscripts n_i then refer to either occupied or unnoccupied states, denoted by i, j and a, b, respectively.

Elimination of the sum over unoccupied states

The evaluation of the density-density response function requires the summation over all unoccupied states for every occupied state. In practice this summation is truncated. However to reach convergence one typically needs to include at least as many unoccupied states as the number of occupied states. For large systems this can become very costly. We can avoid this summation by writing[1]:

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \lim_{\eta\to 0^+} \frac{1}{V_{BZ}} \sum_v \int d\mathbf{k} \langle \phi_{v\mathbf{k}'} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \left[|\Psi^+_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle + |\Psi^-_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle \right]$$

where the summation over v indicates a summation over occupied states only.

$$|\Psi^{\pm}_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle = \sum_{n'} \frac{|\phi_{n'\mathbf{k}}\rangle\langle\phi_{n'\mathbf{k}}| e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} |\phi_{v\mathbf{k}'}\rangle}{\pm\omega - (\epsilon_{n'\mathbf{k}} - \epsilon_{v\mathbf{k}'}) \pm i\eta}$$

This means that we have to solve the following equation

$$\left[-\hat{h}(\mathbf{r}) + \epsilon_{v\mathbf{k}'} \pm \omega \pm i\eta \right] |\Psi^{\pm}_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle = e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |\phi_{v\mathbf{k}'}\rangle$$

Solving this equation requires inversion of the Hamiltonian. Since its kinetic part is local in G space and the potential is local in real space it is would be convenient to solve this equation in mixed space.

Projection onto the unoccupied states

When the frequency goes to zero $\left[-\hat{h}(\mathbf{r}) + \epsilon_{v\mathbf{k}'} \pm \omega \pm i\eta\right]$ diverges. For numerical reasons it is therefore better to project out the occupied states from the Hamiltonian. Our equations then become

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \lim_{\eta\to 0^+} \frac{1}{V_{BZ}} \sum_v \int d\mathbf{k} \langle \phi_{v\mathbf{k}'} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \hat{P} | \left[|\tilde{\Psi}^+_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle + |\tilde{\Psi}^-_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle \right]$$

where $\tilde{\Psi}^+$ and $\tilde{\Psi}^-$ are the solutions of the following equations

$$\begin{aligned}
\left[-\hat{h}(\mathbf{r})\hat{P} + \epsilon_{v\mathbf{k}'} + \omega + i\eta\right] |\tilde{\Psi}^+_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle &= \hat{P} e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |\phi_{v\mathbf{k}'}\rangle \\
\left[-\hat{h}(\mathbf{r})\hat{P} + \epsilon_{v\mathbf{k}'} - \omega - i\eta\right] |\tilde{\Psi}^-_{v\mathbf{k}',\mathbf{q},\mathbf{G}'}(\omega)\rangle &= \hat{P} e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |\phi_{v\mathbf{k}'}\rangle
\end{aligned}$$

and $\hat{P} = 1 - \sum_v |\phi_{v\mathbf{k}}\rangle\langle\phi_{v\mathbf{k}}|$. In this way we can ensure that the method is stable for ω close to zero.

Inversion of the Hamiltonian

The standard sum-over-states approach scales as N^4

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \lim_{\eta\to 0^+} \frac{1}{V_{BZ}} \sum_{v,c} \int_{BZ} d\mathbf{k} \frac{c_{vc\mathbf{kk'}}(\mathbf{G}) c^*_{vc\mathbf{kk'}}(\mathbf{G'})}{\omega - (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k'}}) + i\eta} + c.c.(\mathbf{G} \leftrightarrow \mathbf{G'}, -\omega)$$

where

$$c_{vc\mathbf{kk'}}(\mathbf{G}) = \int d\mathbf{r} e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \phi^*_{v\mathbf{k}}(\mathbf{r}) \phi_{c\mathbf{k'}}(\mathbf{r})$$

Let us now evaluate the scaling of our alternative expression for χ^0. We can rewrite it in the following way

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \lim_{\eta\to 0^+} \frac{1}{V_{BZ}} \sum_{v} \int d\mathbf{k} \int d\mathbf{r} d\mathbf{r'} u^*_{v\mathbf{k'}}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \left[[A^+_v]^{-1}_{\mathbf{rr'}} + [A^-_v]^{-1}_{\mathbf{rr'}} \right] u_{v\mathbf{k'}}(\mathbf{r'}) e^{i\mathbf{G'}\cdot\mathbf{r'}}$$

where $A^{\pm}_{v\mathbf{rr'}}$ is the Fourier transform of

$$A^{\pm}_{v\mathbf{GG''}} = \left[-\tilde{h}_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G''}} + (\epsilon_{v\mathbf{k'}} \pm \omega \pm i\eta)\, \delta_{\mathbf{GG''}} \right]$$

Given the inverse of $A^{\pm}_v$ the scaling for the calculation of χ is $N^3 \log N$ when fast Fourier transforms (FFTs) are used. However the scaling of the inversion itself is N^3 for every occupied state using a standard matrix inversion. An improved scaling can be obtained by evaluating the nabla operator in the Hamiltonian in real space using finite differences. In this way the matrix $A^{\pm}_v$ will be sparse since the potenial part of the Hamiltonian is diagonal in real space.

An iterative Scheme

Alternatively, since our problem is of the form $\langle u|(z-H)^{-1}|v\rangle$ we can use a Lanczos algorithm. Starting from $|q_1\rangle = v$ we can build an orthonormal basis according to

$$b_{i+1}|q_{i+1}\rangle = H|q_i\rangle - a_i|q_i\rangle - b_i|q_{i-1}\rangle$$

where

$$a_i = \langle q_i|\hat{h}|q_i\rangle \quad b_{i+1} = |RHS|$$

Using this basis our problem can be rewritten as

$$\langle u|(z-H)^{-1}|v\rangle = \langle u|A(z-M)^{-1}|e_1\rangle$$

in which M is just a tridiagonal matrix:

$$M = \begin{pmatrix} a_1 & b_2 & 0 & \dots \\ b_2 & a_2 & b_3 & 0 \\ 0 & b_3 & a_3 & b_4 \\ \vdots & & & \ddots \\ \vdots & 0 & b_4 & \end{pmatrix} \qquad A = [q_1, q_2, q_3, \cdots]$$

Although the scaling of this approach is the same as that for the sum-over-states approach (N^4), if it converges fast enough it might give an advantage over the latter. The Lanczos basis can be efficiently evaluated by making use of a mixed-space approach for the Hamiltonian.

Conclusions

Our current methods used for calculations on extended systems need to be reformulated in order to make calculations for (large) finite systems feasible.

The elimination of the sum over unoccupied states in the sum-over-states expression for the density-density response function can reduce the cost of the calculations. However it does not naturally lead to a better scaling.

A better scaling could be obtained by evaluating the nabla operator in the Hamiltonian in real space using finite differences. The evaluation of the response function then requires the inversion of a very sparse matrix.

[1] L. Reining, G. Onida, and R. W. Godby, PRB 56, R4301 (1997).