

Pseudo-Hermitian eigenvalue equations in linear-response electronic-structure theory

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The electronic excitation energies of molecules or solids are most frequently calculated via the linear response of the ground-state wave function to a time-dependent perturbation, as done for example in time-dependent Hartree-Fock theory, time-dependent density-functional theory or the Bethe-Salpeter equation [1], and which leads to pseudo-Hermitian eigenvalue equations [2,3,4,5]. If the response is calculated on a ground state that is properly stable with respect to the perturbation considered, then one can show that the obtained eigenvalue equation is pseudo-Hermitian with respect to a positive-definite matrix, and the excitation energies are thus real, as they should be. However, in practice, approximations are necessarily made and the approximate ground state is sometimes unstable (e.g., with respect to unphysical spin-symmetry breaking), leading to unexploitable imaginary excitation energies. I illustrate this on the simple example of the H_2 molecule [6].

Electronic-structure problem

- We want to solve the **time-independent Schrödinger equation** for the electronic states of atoms, molecules or solids:

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

- The **ground state** is often approximately calculated by a **variational method**, i.e. by minimizing the energy with an approximate wave function $\psi_0(\mathbf{p})$ depending on some optimized parameters \mathbf{p} :

$$E_0 = \min_{\mathbf{p}} \langle \psi_0(\mathbf{p}) | \hat{H} | \psi_0(\mathbf{p}) \rangle$$

Example: Hartree-Fock (HF), multiconfiguration self-consistent field (MCSCF).

- The **excited-state energies** are then often calculated by **linear-response time-dependent perturbation theory** starting from the approximate ground state.

Excitation energies from linear-response theory (1)

- Perturb the system by a time-dependent (e.g., electric) potential:

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

- The approximate ground state $\Psi_0(\mathbf{p}(t))$ evolves in time through the parameters $\mathbf{p}(t)$ according to the Dirac-Frenkel variational principle:

$$\frac{\partial}{\partial p_i^*} \langle \Psi_0(\mathbf{p}(t)) | \hat{H}(t) - i \frac{\partial}{\partial t} | \Psi_0(\mathbf{p}(t)) \rangle = 0 \quad (1)$$

- Expand the wave function around the initial parameters \mathbf{p}^0 :

$$\Psi_0(\mathbf{p}(t)) = \Psi_0(\mathbf{p}^0) + \sum_i \Delta p_i(t) \frac{\partial \Psi_0(\mathbf{p}^0)}{\partial p_i} + \frac{1}{2} \sum_{ij} \Delta p_i(t) \Delta p_j(t) \frac{\partial^2 \Psi_0(\mathbf{p}^0)}{\partial p_i \partial p_j} + \dots$$

where $\Delta \mathbf{p}(t) = \mathbf{p}(t) - \mathbf{p}^0$.

Excitation energies from linear-response theory (2)

We consider the limit of an infinitesimal perturbation $\lambda \rightarrow 0$.

- Using Eq. (1), the first-order parameter variations $\Delta \mathbf{p}$ are given by

$$\mathbf{A} \cdot \Delta \mathbf{p}(t) + \mathbf{B} \cdot \Delta \mathbf{p}(t)^* = i\mathbf{S} \cdot \frac{\partial \Delta \mathbf{p}(t)}{\partial t}$$

where $A_{ij} = \langle \frac{\partial \Psi_0}{\partial p_i} | \hat{H} | \frac{\partial \Psi_0}{\partial p_j} \rangle$, $B_{ij} = \langle \frac{\partial^2 \Psi_0}{\partial p_i \partial p_j} | \hat{H} | \Psi_0 \rangle$ and $S_{ij} = \langle \frac{\partial \Psi_0}{\partial p_i} | \frac{\partial \Psi_0}{\partial p_j} \rangle$

- We look for free-oscillation solutions of the form:

$$\Delta \mathbf{p}(t) = \mathbf{X} e^{-i\omega t} + \mathbf{Y}^* e^{i\omega t}$$

where ω will be an approximation to an excitation energy.

- It leads to a **non-Hermitian generalized eigenvalue equation**:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & -\mathbf{S}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (2)$$

whose solutions come in pairs: excitation energies ω with eigenvectors (\mathbf{X}, \mathbf{Y}) , and de-excitation energies $-\omega$ with eigenvectors $(\mathbf{Y}^*, \mathbf{X}^*)$.

Approximate excitation spectrum may not be real

- **Equation (2) is widely used for computing excitation spectra** in electronic-structure theory (quantum chemistry and condensed-matter physics), and in fact also in nuclear physics. It was demonstrated here for simple variational methods such as HF or MCSCF, but similar equations are obtained for time-dependent density-functional theory (TDDFT) or perturbative methods based on the Bethe-Salpeter equation (BSE). **The generic equation (2) is often called the random phase approximation (RPA).**
- The true excitation energies, $\omega = E_n - E_0$, are of course all real, but in practice, when approximations are used, **one can get unexploitable non-real eigenvalues ω** from the generalized eigenvalue problem (2) because it is non-Hermitian. **These so-called “instabilities” in Eq. (2) plague the computation of excitation spectra in electronic-structure theory.**

Pseudo-Hermiticity of the linear-response problem

- Defining the supermatrices $\mathbb{L} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$ and $\Delta = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & -\mathbf{S}^* \end{pmatrix}$, equation (2) is equivalent to finding the eigenvalues of $\mathbb{H} = \Delta^{-1} \cdot \mathbb{L}$.
- With usual approximations, \mathbf{A} and \mathbf{S} are Hermitian and \mathbf{B} is symmetric. This implies that \mathbb{L} and Δ are Hermitian.
- \mathbb{H} is **pseudo-Hermitian** with respect to \mathbb{L} , i.e. [2,3,4,5]:

$$\mathbb{H}^\dagger = \mathbb{L} \cdot \mathbb{H} \cdot \mathbb{L}^{-1}$$

- Therefore, **if \mathbb{L} is positive definite then \mathbb{H} has only real eigenvalues ω .**

Remark: \mathbb{H} is also pseudo-Hermitian with respect to Δ but Δ is not positive definite.

Stability condition on the ground state

- The expansion of the variational ground-state energy around the minimum is

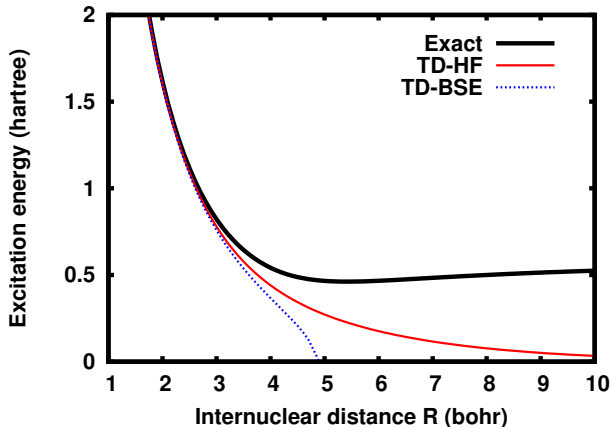
$$E_0(\mathbf{p}) = E_0(\mathbf{p}^{\min}) + \begin{pmatrix} \Delta\mathbf{p}^* & \Delta\mathbf{p} \end{pmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \Delta\mathbf{p} \\ \Delta\mathbf{p}^* \end{pmatrix} + \dots$$

where $\Delta\mathbf{p} = \mathbf{p} - \mathbf{p}^{\min}$.

- \mathbb{L} is thus the Hessian of the ground-state energy at the minimum.
- It follows that if the response is done around a ground state that is a properly stable minimum, \mathbb{L} is positive definite and the linear-response equation (2) gives only real excitation energies.
- In practice, non-real excitation energies can be obtained if either:
 - a non-variational method is used for the ground state.
 - the ground-state variational space is limited by imposing some symmetries (complex-conjugation, spin or spatial symmetry) that could be spontaneously broken due to the chosen approximate wave-function form, but a larger variational space without these symmetry conditions is used in the linear-response calculation.

Example: H_2 molecule in a minimal basis

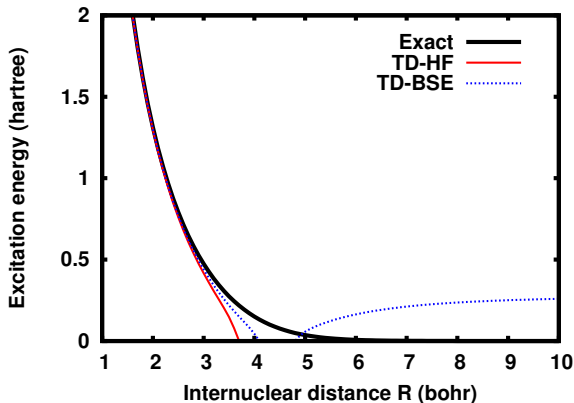
First spin-singlet $^1\Sigma_u^+$ excitation energy:



- The variational TD-HF method gives a real excitation energy at all R (though it is not accurate at large R).
- The non-variational TD-BSE method gives a non-real excitation energy for $R \gtrsim 5$ bohr.

Example: H_2 molecule in a minimal basis

First spin-triplet ${}^3\Sigma_u^+$ excitation energy:



- The TD-HF method gives a non-real excitation energy for $R \gtrsim 3.6$ bohr because the ground-state variational space has been limited by imposing spin-singlet symmetry.
- The TD-BSE method gives a non-real excitation energy between $R \approx 4$ and $R \approx 5$ bohr.

Final remarks and references

- With variational methods, one often faces the following dilemma: either (1) allow unphysical spontaneous symmetry breaking in the ground-state calculation to have only real excitation energies in the linear-response calculation but then the quality of the ground and excited states can be poor, or (2) impose physical symmetries in the ground-state calculation but then the linear-response calculation can give non-real excitation energies for excited states of different symmetry.
- To avoid non-real excitation energies, the Tamm-Dancoff approximation, $\mathbf{B} = \mathbf{0}$, is often used, but it is not always accurate enough.

References:

- [1] G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
- [2] A. Mostafazadeh, J. Math. Phys. 43, 205 (2002).
- [3] A. Mostafazadeh, J. Math. Phys. 43, 2814 (2002).
- [4] A. Mostafazadeh, J. Math. Phys. 43, 3944 (2002).
- [5] M. Grüning, A. Marini, X. Gonze, Comput. Mater. Sci. 50, 2148 (2011).
- [6] E. Rebolini, J. Toulouse, A. Savin, in "Concepts and Methods in Modern Theoretical Chemistry, vol 1: Electronic Structure and Reactivity", S. Ghosh and P. Chattaraj (eds), to appear.