Basis-set correction based on density-functional theory: Linear-response formalism for excited-state energies

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The problem to solve

How to **improve basis-set convergence** of excited-state energies and properties?

Strategy

✓ Development of a hybrid wave-function/density-functional method for basis-set calculations of energies and molecular properties, **the density-based basis-set correction method**:

- We **correct** the **slow convergence of short-range correlation effects** that arises using post Hartree-Fock methods with a functional of the density.
- The self-consistent version of this method was tested for ground-state energies and dipole moments [1, 2].

❑ Here, we present an **extension** of the density-based basis-set correction **to a linear-response formalism**.

General ground-state optimization

- The ground-state energy expression is

$$E^{\mathcal{B}}(\mathbf{p}) = \frac{\langle \bar{\Psi}(\mathbf{p}) | \hat{H} | \bar{\Psi}(\mathbf{p}) \rangle}{\langle \bar{\Psi}(\mathbf{p}) | \bar{\Psi}(\mathbf{p}) \rangle} + \bar{E}^{\mathcal{B}}[\rho_{\bar{\Psi}(\mathbf{p})}]. \tag{1}$$

where $\bar{E}^{\mathcal{B}}[\rho_{\bar{\Psi}(\mathbf{p})}]$ aims **to correct the basis error** and verifies the relation $\bar{E}^{\mathcal{B}}[\rho] \underset{\mathcal{B}\to\text{CBS}}{=} 0$.

- We introduce the intermediate-normalized parametrized wave function

$$|\bar{\Psi}(\mathbf{p})\rangle = \frac{|\Psi(\mathbf{p})\rangle}{\langle \Psi_0 | \Psi(\mathbf{p})\rangle}, \tag{2}$$

where $|\Psi_0\rangle = |\Psi(\mathbf{p}^0)\rangle$ is the current wave function and its derivatives with respect to $\mathbf{p}$ are orthogonal to $|\Psi_0\rangle$:

$$|\bar{\Psi}_I\rangle = \frac{\partial |\bar{\Psi}(\mathbf{p})\rangle}{\partial p_I}\Big|_{\mathbf{p}=\mathbf{p}^0} \; ; \; |\bar{\Psi}_{I,J}\rangle = \frac{\partial^2 |\bar{\Psi}(\mathbf{p})\rangle}{\partial p_I \partial p_J}\Big|_{\mathbf{p}=\mathbf{p}^0}$$

$$\langle \bar{\Psi}_I | \Psi_0 \rangle = 0 \; ; \; \langle \bar{\Psi}_{I,J} | \Psi_0 \rangle = 0.$$

- The ground-state energy is defined through

$$E_0^{\mathcal{B}} = \min_{\mathbf{p}\in\mathbb{C}^M} E^{\mathcal{B}}(\mathbf{p}). \tag{3}$$

Using the Newton-Raphson iterative method, optimal parameters $\mathbf{p}^0$ are found from

$$\begin{bmatrix} \mathsf{A} & \mathsf{B} \\ \mathsf{B}^* & \mathsf{A}^* \end{bmatrix} \begin{bmatrix} \Delta\mathbf{p} \\ \Delta\mathbf{p}^* \end{bmatrix} = - \begin{bmatrix} \mathbf{g} \\ \mathbf{g}^* \end{bmatrix} \tag{4}$$

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

In Eq. (4),

$$g_I = \frac{\partial E^{\mathcal{B}}(\mathbf{p})}{\partial p_I^*}\Big|_{\mathbf{p}=\mathbf{p}^0} = \langle \bar{\Psi}_I | \hat{H}^{\mathcal{B}}_{\text{eff}} | \Psi_0 \rangle \tag{5}$$

$$A_{I,J} = \frac{\partial^2 E^{\mathcal{B}}(\mathbf{p})}{\partial p_I^* \partial p_J}\Big|_{\mathbf{p}=\mathbf{p}^0} = \langle \bar{\Psi}_I | \hat{H}^{\mathcal{B}}_{\text{eff}} - \mathcal{E}_0^{\mathcal{B}} | \bar{\Psi}_J \rangle + K_{I,J}, \tag{6}$$

$$B_{I,J} = \frac{\partial^2 E^{\mathcal{B}}(\mathbf{p})}{\partial p_I^* \partial p_J^*}\Big|_{\mathbf{p}=\mathbf{p}^0} = \langle \bar{\Psi}_{IJ} | \hat{H}^{\mathcal{B}}_{\text{eff}} | \Psi_0 \rangle + L_{I,J}, \tag{7}$$

and

$$\hat{H}^{\mathcal{B}}_{\text{eff}} = \hat{H} + \bar{V}^{\mathcal{B}} \; ; \; \mathcal{E}_0^{\mathcal{B}} = \langle \Psi_0 | \hat{H}^{\mathcal{B}}_{\text{eff}} | \Psi_0 \rangle . \tag{8}$$

General linear-response equations

We consider the time-dependent Hamiltonian $\hat{H}(t)$,

$$\hat{H}(t) = \hat{H} + \hat{V}(t), \tag{9}$$

with the periodic electric-dipole interaction of frequency ω,

$$\hat{V}(t) = -\hat{\mathbf{d}} \cdot \epsilon^+ e^{-i\omega t} - \hat{\mathbf{d}} \cdot \epsilon^- e^{+i\omega t}. \tag{10}$$

To build the linear-response equation, we consider the quasi-energy

$$\mathcal{Q}^{\mathcal{B}} = \frac{1}{T}\int_0^T \left[\frac{\langle \bar{\Psi}(\mathbf{p}(t)) | \hat{H}(t) - i\frac{\partial}{\partial t} | \bar{\Psi}(\mathbf{p}(t)) \rangle}{\langle \bar{\Psi}(\mathbf{p}(t)) | \bar{\Psi}(\mathbf{p}(t)) \rangle} + \bar{E}^{\mathcal{B}}\left[\rho_{\bar{\Psi}(\mathbf{p}(t))}\right] \right]. \tag{11}$$

From $\Delta\mathbf{p}(t) = \mathbf{p}^+ e^{-i\omega t} + \mathbf{p}^- e^{+i\omega t}$, the optimal quasi-energy is defined through

$$\mathcal{Q}_0^{\mathcal{B}} = \underset{(\mathbf{p}^+,\mathbf{p}^-)\in\mathbb{C}^{2M}}{\text{stat}} \mathcal{Q}^{\mathcal{B}} \tag{12}$$

Excitation energies $\omega_n^{\mathcal{B}}$ verify the linear-response equations

$$\begin{bmatrix} \mathsf{A} & \mathsf{B} \\ \mathsf{B}^* & \mathsf{A}^* \end{bmatrix} \begin{bmatrix} \mathsf{X}_n \\ \mathsf{Y}_n \end{bmatrix} = \omega_n^{\mathcal{B}} \begin{bmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{bmatrix} \begin{bmatrix} \mathsf{X}_n \\ \mathsf{Y}_n \end{bmatrix}, \tag{13}$$

where

$$S_{I,J} = \langle \bar{\Psi}_I | \bar{\Psi}_J \rangle, \tag{14}$$

and the excited-state energies are obtained by

$$E_n^{\mathcal{B}} = E_0^{\mathcal{B}} + \omega_n^{\mathcal{B}}. \tag{15}$$

Linear-response equations for configuration interaction

The CI wave function is expanded on a set of Slater determinants Φ_I:

$$|\Psi(\mathbf{p})\rangle = \sum_{I=1}^{M} p_I |\Phi_I\rangle \tag{16}$$

The linear-response (Eq. (13)) matrix elements are re-written as

$$A_{I,J} = \langle \Phi_I | \hat{H}^{\mathcal{B}}_{\text{eff}} - \mathcal{E}_0^{\mathcal{B}} | \Phi_J \rangle + \boxed{K_{I,J}} \tag{17}$$

$$B_{I,J} = \boxed{K_{I,J}} \tag{18}$$

$$S_{I,J} = \delta_{I,J} - c_I c_J \tag{19}$$

with the basis-set correction kernel contribution:

$$K_{I,J} = \sum_{i,j,k,l} \Delta\gamma^I_{i,j} \Delta\gamma^J_{kl} \, \bar{f}^{\mathcal{B}}_{i,j,k,l} \tag{20}$$

with

$$\gamma^I_{i,j} = \langle \Phi_I | \hat{E}_{i,j} | \Psi_0 \rangle - c_I \langle \Psi_0 | \hat{E}_{i,j} | \Psi_0 \rangle , \tag{21}$$

where $\hat{E}_{i,j} = \hat{a}^\dagger_{i\uparrow}\hat{a}_{j\uparrow} + \hat{a}^\dagger_{i\downarrow}\hat{a}_{j\downarrow}$, $|\Psi_0\rangle = \sum_{I=1}^M c_I |\Phi_I\rangle$, and

$$\bar{f}^{\mathcal{B}}_{i,j,k,l} = \int_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \; \bar{f}^{\mathcal{B}}[\rho_{\Psi_0}](\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r})\phi_k(\mathbf{r}')\phi_l(\mathbf{r}'), \tag{22}$$

where

$$\bar{f}^{\mathcal{B}}[\rho_{\Psi_0}](\mathbf{r},\mathbf{r}') = \frac{\partial^2 \bar{E}^{\mathcal{B}}[\rho]}{\partial\rho(\mathbf{r})\partial\rho(\mathbf{r}')}. \tag{23}$$

Tests on the 1D model system

- 2 electrons in a 1D space in a harmonic potential with a delta electron-electron interaction:

$$\hat{H} = \sum_{i\in\{1,2\}} \left(-\frac{1}{2}\frac{\partial^2}{\partial x_i^2} + \frac{1}{2}\omega_0^2 x_i^2 \right) + \delta(x_1 - x_2) \tag{24}$$

- FCI with a Hermite-Gaussian basis set
- A Local-Density-Approximation (LDA) to correct for incomplete basis-set [3]

$$\bar{E}^{\mathcal{B}}_{\text{LDA}}[\rho] = \int \mathrm{d}x \; \rho(x)\bar{\epsilon}^{\mathcal{B}}(\rho(x)). \tag{25}$$

The energy per particle is expressed as a numerical fit,

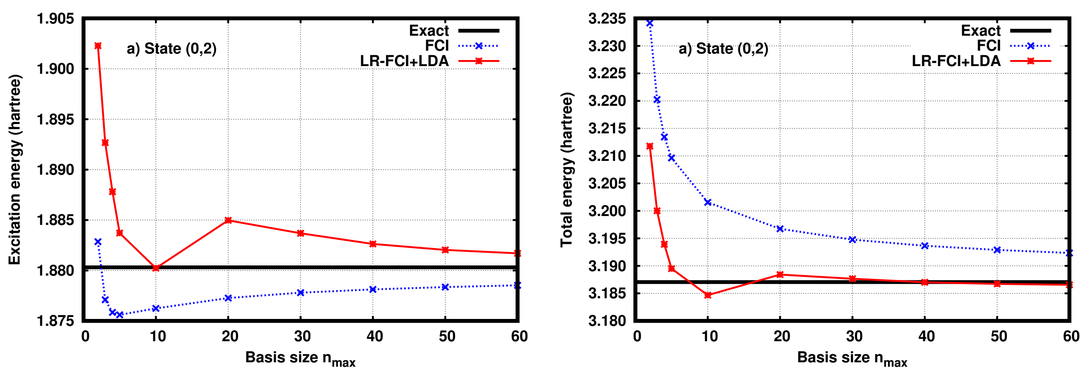
$$\bar{\epsilon}^{\mathcal{B}}(\rho) \simeq \frac{\sum_{i=0}^4 a_i^{\mathcal{B}} \rho^i}{1 + \sum_{j=1}^4 b_j^{\mathcal{B}} \rho^j}, \tag{26}$$

to easily compute the needed derivatives:

$$\bar{v}^{\mathcal{B}}_{\text{LDA}}[\rho](x) = \bar{\epsilon}^{\mathcal{B}}(\rho(x)) + \rho(x)\frac{\mathrm{d}\,\bar{\epsilon}^{\mathcal{B}}(\rho)}{\mathrm{d}\rho}\Big|_{\rho=\rho(x)} \tag{27}$$

$$\bar{f}^{\mathcal{B}}_{\text{LDA}}[\rho](x,x') = \left[2\frac{\mathrm{d}\,\bar{\epsilon}^{\mathcal{B}}(\rho)}{\mathrm{d}\rho}\Big|_{\rho=\rho(x)} + \rho(x)\frac{\mathrm{d}^2\bar{\epsilon}^{\mathcal{B}}(\rho)}{\mathrm{d}\rho^2}\Big|_{\rho=\rho(x)} \right] \delta(x-x'). \tag{28}$$

Example on the first excited-state energy of the 1D system:



- ✗ No improvement of the basis convergence of the excitation energies.
- ✓ Great improvement of the basis convergence of the excited-state energies.

Ongoing : applications on real systems

- Improvement of the approximation used for the density functional.
- Perturbatively selected configuration interaction state (CIPSI) to build a set of determinants for the linear response equations.
- Implementation of the basis-set correction kernel contribution.
- Tests on atomic and molecular systems.

Softwares

- A Fortran home-made code for a 1D model system with Hartree-Fock, Full CI and density-based basis-set correction algorithms **for method development**.
- Quantum Package 2.0 **for applications on real systems**.

References

[1] E. Giner, D. Traore, B. Pradines and J. Toulouse, The Journal of Chemical Physics **155**, 044109 (2021).
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[3] D. Traore, E. Giner and J. Toulouse, The Journal of Chemical Physics **156**, 044113 (2022).