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RESEARCH ARTICLE

Excited states from range-separated density-functional perturbation theory

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We explore the possibility of calculating electronic excited states by using perturbation theory along a range-separated adiabatic connection. Starting from the energies of a partially interacting Hamiltonian, a first-order correction is defined with two variants of perturbation theory: a straightforward perturbation theory, and an extension of the Görling–Levy one that has the advantage of keeping the ground-state density constant at each order in the perturbation. Only the first, simpler, variant is tested here on the helium and beryllium atoms and on the hydrogene molecule. The first-order correction within this perturbation theory improves significantly the total ground- and excited-state energies of the different systems. However, the excitation energies mostly deteriorate with respect to the zeroth-order ones, which may be explained by the fact that the ionization energy is no longer correct for all interaction strengths. The second (Görling–Levy) variant of the perturbation theory should improve these results but has not been tested yet along the range-separated adiabatic connection.

Keywords: Excitation energies; Range separation; Perturbation theory; Adiabatic connection

1. Introduction

In density-functional theory (DFT) of quantum electronic systems, the most widely used approach for calculating excitation energies is nowadays linear-response time-dependent density-functional theory (TDDFT) (see, e.g., Refs. [1, 2]). However, in spite of many successes, when applied with the usual adiabatic semilocal approximations, linear-response TDDFT has serious limitations for describing systems with static (or strong) correlation [3], double or multiple excitations [4], and Rydberg and charge-transfer excitations [5, 6]. Besides, the Hohenberg–Kohn theorem [7] states that the time-independent ground-state density contains all the information about the system implying that time dependence is in principle not required to describe excited states.

Several time-independent DFT approaches for calculating excitation energies exist and are still being developed. A first strategy consists in simultaneously optimizing an ensemble of states. Such an ensemble DFT was pioneered by Theophilou [8] and by Gross, Oliveira and Kohn [9] and is still a subject of research [10–13], but it is hampered by the absence of appropriate approximate ensemble functionals. A

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second strategy consists in self-consistently optimizing a single excited state. This approach was started by Gunnarsson and Lundqvist [14], who extended ground-state DFT to the lowest-energy state in each symmetry class, and developed into the pragmatic (multiplet-sum) ΔSCF method [15, 16] (still in use today [17]) and related methods [18–20]. Great efforts have been made by Nagy, Görling, Levy, Ayers and others to formulate a rigorous self-consistent DFT of an arbitrary individual excited state [21–33] but a major difficulty is the need to develop approximate functionals for a specific excited state (see Ref. [34] for a proposal of such excited-state functionals). A third strategy, first proposed by Grimme, consists in using configuration-interaction (CI) schemes in which modified Hamiltonian matrix elements include information from DFT [35–38].

Finally, a fourth possible approach, proposed by Görling [39], is to calculate the excitation energies from Görling–Levy (GL) perturbation theory [40, 41] along the adiabatic connection using the non-interacting Kohn–Sham (KS) Hamiltonian as the zeroth-order Hamiltonian. In this approach, the zeroth-order approximation to the exact excitation energies is provided by KS orbital energy differences (which, for accurate KS potentials, is known to be already a fairly good approximation [42–44]). It can be improved upon by perturbation theory at a given order in the coupling constant of the adiabatic connection. Filippi, Umrigar, and Gonze [45] showed that the GL first-order corrections provide a factor of two improvement on the KS zeroth-order excitation energies for the He, Li^+, and Be atoms when using accurate KS potentials. For (nearly) degenerate states, Zhang and Burke [46] proposed to use degenerate second-order GL perturbation theory, showing that it works well for a simple one-dimensional model. This approach is conceptually simple as it uses the standard adiabatic connection along which the ground-state density is kept constant (in contrast to approaches introducing generalized adiabatic connections keeping an excited-state density constant [21, 22, 24, 29]). In spite of promising early results, this approach has not been pursued further, perhaps because it can be considered an approximation to TDDFT [47].

In this work, we explore further this density-functional perturbation-theory approach for calculating excitation energies, introducing one key modification in comparison to the earlier work of Refs. [39, 45]: As a zeroth-order Hamiltonian, instead of using the non-interacting KS Hamiltonian, we use a *partially interacting Hamiltonian* incorporating the *long-range* part only of the Coulomb electron–electron interaction, corresponding to an intermediate point along a range-separated adiabatic connection [48–53]. The partially interacting zeroth-order Hamiltonian is of course closer to the exact Hamiltonian than is the non-interacting KS Hamiltonian, thereby putting less demand on the perturbation theory. In fact, the zeroth-order Hamiltonian can already incorporate some static correlation.

The downside of this approach is that a many-body method such as CI theory is required to generate the eigenstates and eigenvalues of the zeroth-order Hamiltonian. However, if the partial electron–electron interaction is only a relatively weak long-range interaction, we expect a faster convergence of the eigenstates and eigenvalues with respect to the one- and many–electron CI expansion than for the full Coulomb interaction [52, 54], so that a small CI or multi-configuration self-consistent field (MCSCF) description would be sufficiently accurate.

When using a semi-local density-functional approximation for the effective potential of the range-separated adiabatic connection, the presence of an explicit long-range electron–electron interaction in the zeroth-order Hamiltonian has the additional advantage of preventing the collapse of the high-lying Rydberg excitation energies [48, 55, 56]. In contrast to adiabatic TDDFT, double and multiple excitations can be described with this density-functional perturbation-theory approach,

although this possibility was not explored in Refs. [39, 45]. Finally, approximate excited-state wave functions are obtained in the course of the calculations, which is useful for interpretative analysis and for the calculation of properties. We envisage using this density-functional perturbation theory to calculate excited states after a range-separated ground-state calculation combining a long-range CI [57, 58] or long-range MCSCF [59, 60] treatment with a short-range density functional. This would be a simpler alternative to linear-response range-separated MCSCF theory [61, 62] for calculations of excitation energies.

In this work, we study in detail two variants of range-separated density-functional perturbation theory based either on the Rayleigh–Schrödinger (RS) or Görling–Levy (GL) perturbation theories and test the first, simpler variant on the He and Be atoms and the H_2 molecule, performing accurate calculations along a range-separated adiabatic connection without introducing density-functional approximations.

The two variants of the range-separated perturbation theory are presented in Section 2. Except for the finite basis approximation, no other approximation is introduced and the computational details can be found in Section 3. Finally, the results obtained for the He and Be atoms and for the H_2 molecule are discussed in Section 4. Section 5 contains our conclusions.

2.   Range-separated density-functional perturbation theory

2.1.   *Range-separated ground-state density-functional theory*

In range-separated DFT (see, e.g., Ref. [52]), the exact ground-state energy of an N-electron system is obtained by the following minimization over normalized multi-determinantal wave functions Ψ

$$
E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} | \Psi \rangle + \bar{E}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\Psi}] \right\},
\tag{1}
$$

where we have introduced the kinetic-energy operator $\hat{T}$, the nuclear attraction operator $\hat{V}_{\mathrm{ne}} = \int v_{\mathrm{ne}}(\mathbf{r})\hat{n}(\mathbf{r})\mathrm{d}\mathbf{r}$ written in terms of the density operator $\hat{n}(\mathbf{r})$, a long-range (lr) electron–electron interaction

$$
\hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} = \frac{1}{2} \iint w_{\mathrm{ee}}^{\mathrm{lr},\mu}(r_{12})\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2,
\tag{2}
$$

written in terms of the error-function interaction $w_{\mathrm{ee}}^{\mathrm{lr},\mu}(r) = \mathrm{erf}(\mu r)/r$ and the pair-density operator $\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2)$ and finally the corresponding complement short-range (sr) Hartree–exchange–correlation density functional $\bar{E}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\Psi}]$ evaluated at the density of Ψ. The density and pair density are obtained as expectation values of the density and pair density operators respectively

$$
n_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle,
\tag{3}
$$

$$
n_{2,\Psi}(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi | \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) | \Psi \rangle.
\tag{4}
$$

The parameter μ in the error function controls the separation range, with $1/\mu$ acting as a smooth cut-off radius.

The Euler–Lagrange equation for the minimization of Eq. (1) leads to the (self-

consistent) eigenvalue equation

$$\hat{H}^{\mathrm{lr},\mu}|\Psi_0^\mu\rangle = \mathcal{E}_0^\mu|\Psi_0^\mu\rangle, \tag{5}$$

where Ψ_0^μ and $\mathcal{E}_0^\mu$ are taken as the ground-state wave function and associated energy of the partially interacting Hamiltonian (with an explicit long-range electron–electron interaction)

$$\hat{H}^{\mathrm{lr},\mu} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{\bar{V}}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}, \tag{6}$$

which contains the short-range Hartree–exchange–correlation potential operator,

$$\hat{\bar{V}}_{\mathrm{H}xc}^{\mathrm{sr},\mu} = \int \bar{v}_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n_0](\mathbf{r})\hat{n}(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{7}$$

where $\bar{v}_{\mathrm{H}xc}^{\mathrm{sr},\mu}[n](\mathbf{r}) = \delta\bar{E}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n]/\delta n(\mathbf{r})$, evaluated at the ground-state density of the physical system $n_0(\mathbf{r}) = \langle\Psi_0^\mu|\hat{n}(\mathbf{r})|\Psi_0^\mu\rangle$ for all μ.

For $\mu = 0$, the Hamiltonian $\hat{H}^{\mathrm{lr},\mu}$ of Eq. (6) reduces to the standard non-interacting KS Hamiltonian, $\hat{H}^{\mathrm{lr},\mu=0} = \hat{H}^{\mathrm{KS}}$, whereas, for $\mu \to \infty$, it reduces to the physical Hamiltonian $\hat{H}^{\mathrm{lr},\mu\to\infty} = \hat{H}$. Therefore, when varying the parameter μ between these two limits, the Hamiltonian $\hat{H}^{\mathrm{lr},\mu}$ defines a range-separated adiabatic connection, linking the non-interacting KS system to the physical system with the ground-state density kept constant (assuming that the exact short-range Hartree–exchange–correlation potential $\bar{v}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}(\mathbf{r})$ is used).

2.2.   *Excited states from perturbation theory*

Excitation energies in range-separated DFT can be obtained by linear-response theory starting from the (adiabatic) time-dependent generalization of Eq. (1) [63], where the excited states and their associated energies are obtained from time-independent many-body perturbation theory. In standard KS theory, the single-determinant eigenstates and associated energies of the non-interacting KS Hamiltonian,

$$\hat{H}^{\mathrm{KS}}|\Phi_k^{\mathrm{KS}}\rangle = \mathcal{E}_k^{\mathrm{KS}}|\Phi_k^{\mathrm{KS}}\rangle, \tag{8}$$

where $\hat{H}^{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{Hxc}}$, give a first approximation to the eigenstates and associated energies of the physical Hamiltonian. To calculate excitation energies, two variants of perturbation theory using the KS Hamiltonian as zeroth-order Hamiltonian have been proposed [39, 45]. We here extend these two variants of perturbation theory to range-separated DFT. As a first approximation, it is natural to use the excited-state wave functions and energies of the long-range interacting Hamiltonian

$$\hat{H}^{\mathrm{lr},\mu}|\Psi_k^\mu\rangle = \mathcal{E}_k^\mu|\Psi_k^\mu\rangle, \tag{9}$$

where $\hat{H}^{\mathrm{lr},\mu}$ is the Hamiltonian of Eq. (6) with the short-range Hartree–exchange–correlation potential $\hat{\bar{V}}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}$ evaluated at the *ground-state density* n_0. These excited-state wave functions and energies can then be improved upon by defining perturbation theories in which the Hamiltonian $\hat{H}^{\mathrm{lr},\mu}$ is used as the zeroth-order Hamiltonian.

2.2.1. RS-based variant of perturbation theory

The simplest way of defining such a perturbation theory is to introduce the following Hamiltonian dependent on the coupling constant λ

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\mathrm{lr},\mu} + \lambda \hat{W}^{\mathrm{sr},\mu}, \tag{10}$$

where the short-range perturbation operator is

$$\hat{W}^{\mathrm{sr},\mu} = \hat{W}^{\mathrm{sr},\mu}_{\mathrm{ee}} - \hat{\bar{V}}^{\mathrm{sr},\mu}_{\mathrm{Hxc}}, \tag{11}$$

with the short-range electron–electron interaction

$$\hat{W}^{\mathrm{sr},\mu}_{\mathrm{ee}} = (1/2) \iint w^{\mathrm{sr},\mu}_{\mathrm{ee}}(r_{12}) \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \tag{12}$$

defined with the complementary error-function interaction $w^{\mathrm{sr},\mu}_{\mathrm{ee}}(r) = \mathrm{erfc}(\mu r)/r$. When varying λ, Eq. (10) sets up an adiabatic connection linking the long-range interacting Hamiltonian at $\hat{H}^{\mu,\lambda=0} = \hat{H}^{\mathrm{lr},\mu}$, to the physical Hamiltonian $\hat{H}^{\mu,\lambda=1} = \hat{H}$, for all μ. Importantly, the ground-state density is *not kept constant* along this adiabatic connection.

The exact eigenstates and associated eigenvalues of the physical Hamiltonian can be obtained by standard RS perturbation theory—that is, by Taylor expanding the eigenstates and eigenvalues of the Hamiltonian $\hat{H}^{\mu,\lambda}$ in λ and setting $\lambda = 1$:

$$|\Psi_k\rangle = |\Psi_k^\mu\rangle + \sum_{n=1}^\infty |\Psi_k^{\mu,(n)}\rangle, \tag{13a}$$

$$E_k = \mathcal{E}_k^\mu + \sum_{n=1}^\infty E_k^{\mu,(n)}, \tag{13b}$$

where $\Psi_k^\mu \equiv \Psi_k^{\mu,(0)}$ and $\mathcal{E}_k^\mu \equiv E_k^{\mu,(0)}$ act as zeroth-order eigenstates and energies. Using orthonormalized zeroth-order eigenstates $\langle \Psi_k^\mu | \Psi_l^\mu \rangle = \delta_{kl}$ and assuming non-degenerate zeroth-order eigenstates, the first-order energy correction for the state k becomes

$$E_k^{\mu,(1)} = \langle \Psi_k^\mu | \hat{W}^{\mathrm{sr},\mu} | \Psi_k^\mu \rangle. \tag{14}$$

As usual, the zeroth+first-order energy is simply the expectation value of the physical Hamiltonian over the zeroth-order eigenstate:

$$E_k^{\mu,(0+1)} = \mathcal{E}_k^\mu + E_k^{\mu,(1)} = \langle \Psi_k^\mu | \hat{H} | \Psi_k^\mu \rangle. \tag{15}$$

This expression is a multi-determinantal extension of the exact-exchange KS energy expression for the state k, proposed and studied for the ground state in Refs. [64–66]. The second-order energy correction is given by

$$E_k^{\mu,(2)} = -\sum_{l \neq k} \frac{|\langle \Psi_l^\mu | \hat{W}^{\mathrm{sr},\mu} | \Psi_k^\mu \rangle|^2}{\mathcal{E}_l^\mu - \mathcal{E}_k^\mu}, \tag{16}$$

where the first-order wave-function correction is given by (using intermediate normalization so that $\langle \Psi_k^\mu | \Psi_k^{\mu,(n)} \rangle = 0$ for all $n \geq 1$)

$$|\Psi_k^{\mu,(1)}\rangle = -\sum_{l \neq k} \frac{\langle \Psi_l^\mu | \hat{W}^{\mathrm{sr},\mu} | \Psi_k^\mu \rangle}{\mathcal{E}_l^\mu - \mathcal{E}_k^\mu} |\Psi_l^\mu\rangle. \qquad (17)$$

For $\mu = 0$, this perturbation theory reduces to the first variant of the KS perturbation theory studied by Filippi *et al.*, see Eq. (5) of Ref. [45].

To understand the numerical results in Section 4, we now consider how the zeroth+first-order energies with respect μ near the KS system ($\mu = 0$) and near the physical system ($\mu \to \infty$). The total energies up to the first order of perturbation theory are given by the expectation value of the full Hamiltonian over the zeroth-order wave functions in Eq (14). Using the Taylor expansion of the wave function $\Psi_k^\mu = \Phi_k^{\mathrm{KS}} + \mu^3 \Psi_k^{(3)} + \mathcal{O}(\mu^5)$ around the KS wave function [53], the zeroth+first-order energies are thus given by

$$E_k^{\mu,(0+1)} = \langle \Phi_k^{\mathrm{KS}} | \hat{H} | \Phi_k^{\mathrm{KS}} \rangle + 2\mu^3 \langle \Phi_k^{\mathrm{KS}} | \hat{H} | \Psi_k^{(3)} \rangle + \mathcal{O}(\mu^5), \qquad (18)$$

where $\Psi_k^{(3)}$ is the contribution entering at the third power of μ in the zeroth-order wave function.

From the asymptotic expansion of the wave function $\Psi_k^\mu = \Psi_k + \mu^{-2} \Psi_k^{(-2)} + \mathcal{O}(\mu^{-3})$, which is valid almost everywhere when $\mu \to \infty$ (the electron-electron coalescence needs to be treated carefully) [53], the first correction to the zeroth+first-order energies are seen to enter at the fourth power in μ

$$E_k^{\mu,(0+1)} = E_k + \frac{1}{\mu^4} E_k^{(0+1,-4)} + \mathcal{O}\left(\frac{1}{\mu^6}\right), \qquad (19)$$

where $E_k^{(0+1,-4)}$ is the contribution entering at the fourth power of $1/\mu$.

2.2.2. GL-based variant of perturbation theory

A second possibility is to define a perturbation theory based on a slightly more complicated adiabatic connection, in which the ground-state density is *kept constant* between the long-range interacting Hamiltonian and the physical Hamiltonian, see Appendix A. The Hamiltonian of Eq. (10) is then replaced by

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\mathrm{lr},\mu} + \lambda \hat{W}^{\mathrm{sr},\mu} - \hat{V}_{\mathrm{c,md}}^{\mathrm{sr},\mu,\lambda}, \qquad (20)$$

where $\hat{W}^{\mathrm{sr},\mu}$ is now defined as

$$\hat{W}^{\mathrm{sr},\mu} = \hat{W}_{\mathrm{ee}}^{\mathrm{sr},\mu} - \hat{V}_{\mathrm{Hx,md}}^{\mathrm{sr},\mu}, \qquad (21)$$

in terms of a short-range "multi-determinantal (md) Hartree–exchange" potential operator

$$\hat{V}_{\mathrm{Hx,md}}^{\mathrm{sr},\mu} = \int \frac{\delta E_{\mathrm{Hx,md}}^{\mathrm{sr},\mu}[n_0]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \qquad (22)$$

and a short-range "multi-determinantal correlation" potential operator

$$\hat{V}_{c,md}^{sr,\mu,\lambda} = \int \frac{\delta E_{c,md}^{sr,\mu,\lambda}[n_0]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \, d\mathbf{r}, \tag{23}$$

that depends *non-linearly* on λ so that the ground-state density n_0 is kept constant for all μ and λ. The density functionals $E_{Hx,md}^{sr,\mu}[n]$ and $E_{c,md}^{sr,\mu,\lambda}[n]$ are defined in Appendix A.

One can show that, for non-degenerate ground-state wave functions Ψ_0^μ, the expansion of $\hat{V}_{c,md}^{sr,\mu,\lambda}$ in λ for $\lambda \to 0$ starts at second order:

$$\hat{V}_{c,md}^{sr,\mu,\lambda} = \lambda^2 \, \hat{V}_{c,md}^{sr,\mu,(2)} + \cdots . \tag{24}$$

Hence, the Hamiltonian of Eq. (20) properly reduces to the long-range Hamiltonian at $\lambda = 0$, $\hat{H}^{\mu,\lambda=0} = \hat{H}^{lr,\mu}$, whereas, at $\lambda = 1$, it correctly reduces to the physical Hamiltonian, $\hat{H}^{\mu,\lambda=1} = \hat{H}$. This is so because the short-range Hartree–exchange–correlation potential in the Hamiltonian $\hat{H}^{lr,\mu}$ can be decomposed as

$$\hat{\bar{V}}_{Hxc}^{sr,\mu} = \hat{V}_{Hx,md}^{sr,\mu} + \hat{\bar{V}}_{c,md}^{sr,\mu}, \tag{25}$$

where $\hat{\bar{V}}_{c,md}^{sr,\mu} = \hat{V}_{c,md}^{sr,\mu,\lambda=1}$ is canceled by the perturbation terms for $\lambda = 1$. Equation (25) corresponds to an alternative decomposition of the short-range Hartree–exchange–correlation energy into "Hartree–exchange" and "correlation" contributions based on the multi-determinantal wave function Ψ_0^μ instead of the single-determinant KS wave function Φ_0^{KS} [64–66], which is more natural in range-separated DFT. This decomposition is especially relevant here since it separates the perturbation into a "Hartree–exchange" contribution that is linear in λ and a "correlation" contribution containing all the higher-order terms in λ.

As before, the first-order energy correction is given by Eq. (14) but with the perturbation operator of Eq. (21), yielding the following energy up to first order:

$$E_k^{\mu,(0+1)} = \mathcal{E}_k^\mu + E_k^{\mu,(1)} = \langle \Psi_k^\mu | \hat{H} + \hat{\bar{V}}_{c,md}^{sr,\mu} | \Psi_k^\mu \rangle. \tag{26}$$

The second-order energy correction of Eq. (16) becomes

$$E_k^{\mu,(2)} = -\sum_{l \neq k} \frac{|\langle \Psi_l^\mu | \hat{W}^{sr,\mu} | \Psi_k^\mu \rangle|^2}{\mathcal{E}_l^\mu - \mathcal{E}_k^\mu} - \langle \Psi_k^\mu | \hat{V}_{c,md}^{sr,\mu,(2)} | \Psi_k^\mu \rangle, \tag{27}$$

whereas the expression of the first-order wave function correction is still given by Eq. (17) but with the perturbation operator of Eq. (21).

For $\mu = 0$, this density-fixed perturbation theory reduces to the second variant of the KS perturbation theory proposed by Görling [39] and studied by Filippi *et al.* [Eq. (6) of Ref. [45]], which is simply the application of GL perturbation theory [40, 41] to excited states. In Ref. [45], it was found that the first-order energy corrections in density-fixed KS perturbation theory provided on average a factor of two improvement on the KS zeroth-order excitation energies for the He, Li$^+$, and Be atoms when using accurate KS potentials. By contrast, the first-order energy corrections in the first variant of KS perturbation theory, without a fixed density, deteriorated on average the KS excitation energies.

The good results obtained with the second variant of KS perturbation theory may be understood from that fact that, in GL perturbation theory, the ionization potential remains exact to all orders in λ. In fact, this nice feature of GL theory holds also with range separation, so that the GL-based variant of range-separated perturbation theory should in principle be preferred. However, it requires the separation of the short-range Hartree–exchange–correlation potential into the "multi-determinantal Hartree–exchange" and "multi-determinantal correlation" contributions (according to Eq. (25)), which we have not done for accurate potentials or calculations along the double adiabatic connection with a partial interaction defined by $\hat{W}_{ee}^{lr,\mu} + \lambda \hat{W}_{ee}^{sr,\mu}$ (cf. Appendix A). We therefore consider only the RS-based variant of range-separated perturbation theory here but note that the GL-based variant can be straightforwardly applied with density-functional approximations—using, for example, the local-density approximation that has been constructed for the "multi-determinantal correlation" functional [64, 67].

3.   Computational details

Calculations were performed for the He and Be atoms and the H_2 molecule with a development version of the DALTON program [68], see Refs. [69–71]. Following the same settings as in Ref. [53], a full CI (FCI) calculation was first carried out to get the exact ground-state density within the basis set considered. Next, a Lieb optimization of the short-range potential $v^{sr,\mu}(\mathbf{r})$ was performed to reproduce the FCI density with the long-range electron–electron interaction $w_{ee}^{lr,\mu}(r_{12})$. Then, an FCI calculation was done with the partially-interacting Hamiltonian constructed from $w_{ee}^{lr,\mu}(r_{12})$ and $v^{sr,\mu}(\mathbf{r})$ to obtain the zeroth-order energies and wave functions according to Eq. (9). Finally, the zeroth+first order energies were calculated according to Eq. (15). The second-order correction of Eq. (16) is not calculated in this work. The basis sets used were: uncontracted t-aug-cc-pV5Z for He, uncontracted d-aug-cc-pVDZ for Be, and uncontracted d-aug-cc-pVTZ for H_2.

4.   Results and discussion

All the zeroth-order curves shown hereinafter correspond to the curves of Ref. [53] as the partially interacting Hamiltonian act as starting point for the perturbation theory.

4.1.   *Helium atom*

The ground- and excited-state total energies to first order along the range-separated adiabatic connection of helium are shown in Figure 1. In the KS limit, when $\mu = 0$, the total energies are significantly improved with respect to the zeroth-order ones. In fact, as shown for the ground-state energy, the zeroth-order total energies are off by approximately 1.2 hartree with respect to the energies of the physical system. When the first-order correction is added, the error becomes smaller than 0.06 hartree for all states. Moreover, the singlet and triplet excited-state energies are no longer degenerate. With increasing range-separation parameter μ, a faster convergence towards the total energies of the physical system is also observed at first order for all states.

The description of the total energies is therefore much improved with the addition of the first-order correction. The linear term in μ present in the zeroth-order total
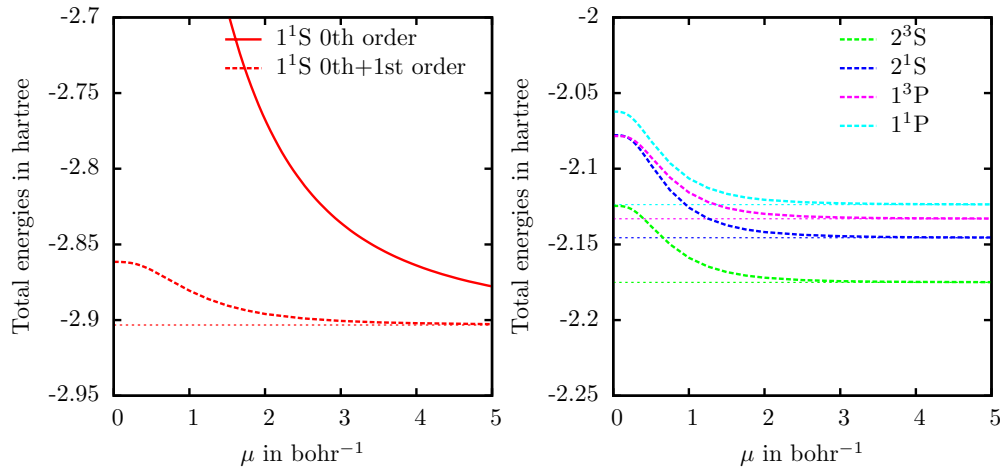
Figure 1. Zeroth+first-order ground- (left) and excited-state (right) total energies $E_k^{\mu,(0+1)}$ (in hartree) of the helium atom as a function of μ (in bohr^{-1}). The zeroth-order energy $\mathcal{E}_0^\mu$ is recalled for the ground state in plain line and the total energies of the physical system E_k are plotted as horizontal dotted lines.
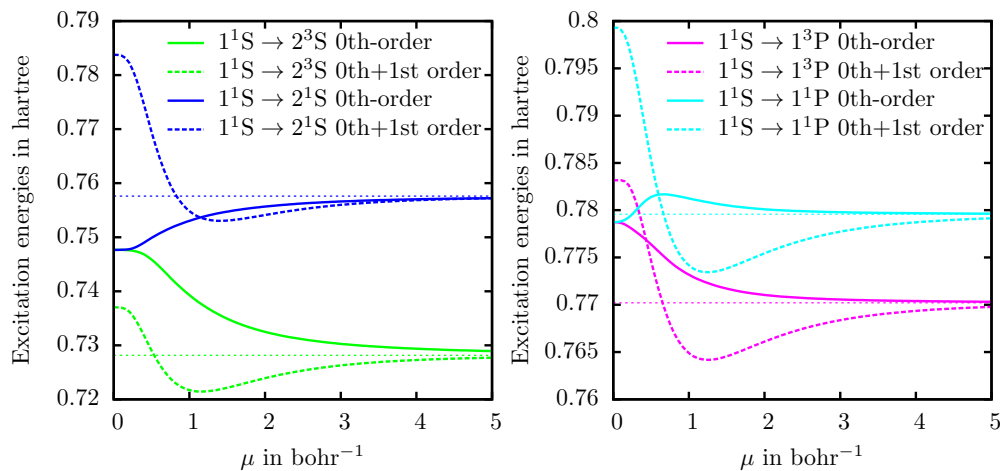

Figure 2. Zeroth-order (plain line) excitation energies $\Delta\mathcal{E}_k^\mu = \mathcal{E}_k^\mu - \mathcal{E}_0^\mu$ and zeroth+first-order (dashed line) excitation energies $\Delta E_k^{\mu,(0+1)} = E_k^{\mu,(0+1)} - E_0^{\mu,(0+1)}$ (in hartree) of the helium atom as a function of μ (in bohr^{-1}). The excitation energies of the physical system $\Delta E_k = E_k - E_0$ are plotted as horizontal dotted lines.

energies [53] vanishes for the zeroth+first order total energies, which instead depend on the the third power of μ for small μ (cf. Eq. (18)). At large μ, the error relative to the physical energies enters as $1/\mu^4$ rather than as $1/\mu^2$ in the zeroth-order case, explaining the observed faster convergence of the first-order energies.

The excitation energies of the helium atom correct to zeroth and first orders are plotted in Figure 2. As previously noted, at $\mu = 0$, the degeneracy of the zeroth-order singlet and triplet excitation energies is lifted by the first-order correction. However, the excitation energies correct to first order overestimate the physical excitation energies by 0.1–0.2 hartree so that the error is actually larger than at zeroth order. For the $1^1S \to 1^3P$ excitation energy, the correction is even going in the wrong direction and the singlet–triplet splitting is too large by about a factor 1.5.

When the extreme long-range part of the Coulombic interaction is switched on with positive μ close to 0, this initial overestimation is corrected. In fact, for small μ, all excitation energies decrease in the third power of μ, in agreement with Eq. (18). When $\mu \simeq 0.5 - 1$, this correction becomes too large and the excitation energies of the partially interacting system become lower than their fully interacting limits.

As μ increases further so that more interaction is included, the excitation energies converge toward their fully interacting values from below. The zeroth-order excitation energies, which do not oscillate for small μ, converge monotonically toward their physical limit and are on average more accurate than the zeroth+first order excitation energies. In short, the first-order correction does not improve excitation energies, although total energies are improved.

The inability of the first-order correction to improve excitation energies should be connected to the fact that, since the ground-state density is not kept constant at each order in the perturbation, the ionization potential is no longer constant to first order along the adiabatic connection. This behavior results in an unbalanced treatment of the ground and excited states. Moreover, high-energy Rydberg excitation energies should be even more sensitive to this effect, as observed for transitions to the P state. The second GL-based variant of perturbation theory should correct this behavior by keeping the density constant at each order, as shown in the KS case [41, 45].

4.2. Beryllium atom

When the first-order perturbation correction is applied to the ground-state and valence-excited states of beryllium, total energies are again improved (not illustrated here). In Figure 3, we have plotted the zeroth- and first-order valence excitation energies of beryllium against the range-separation parameter μ.

Since valence excitation energies should be less sensitive to a poor description of the ionization energy than Rydberg excitation energies, the first-order correction should work better for the beryllium valence excitations than for the helium Rydberg excitations. However, although the singlet excitation energy of beryllium is improved at $\mu = 0$ at first order, the corresponding triplet excitation energy is not. In fact, whereas the triplet excitation energy is overestimated at zeroth order, it is underestimated by about the same amount at first order.

As the interaction is switched on, a bump is observed for small μ for the singlet excitation energy but not the triplet excitation energy, which converges monotonically to its physical limit. The convergence of the excitation energies with μ is improved by the first-order excitation energies, especially in the singlet case.
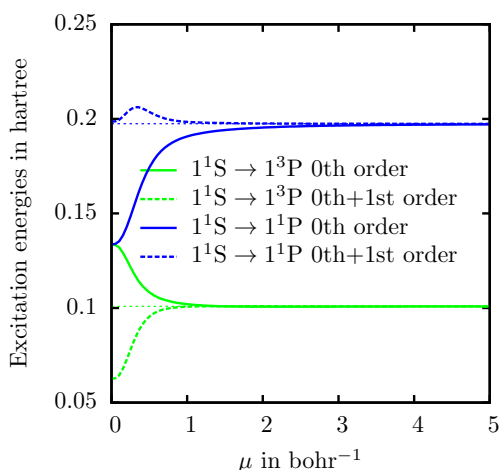

Figure 3.   Valence excitation energies of the beryllium atom (in hartree) at zeroth order $\Delta\mathcal{E}_k^{\mu}$ (plain line) and zeroth+first order $\Delta E_k^{\mu,(0+1)}$ (dashed line), as a function of μ (in bohr^{-1}). The excitation energies of the physical system ΔE_k are plotted as horizontal dotted lines.
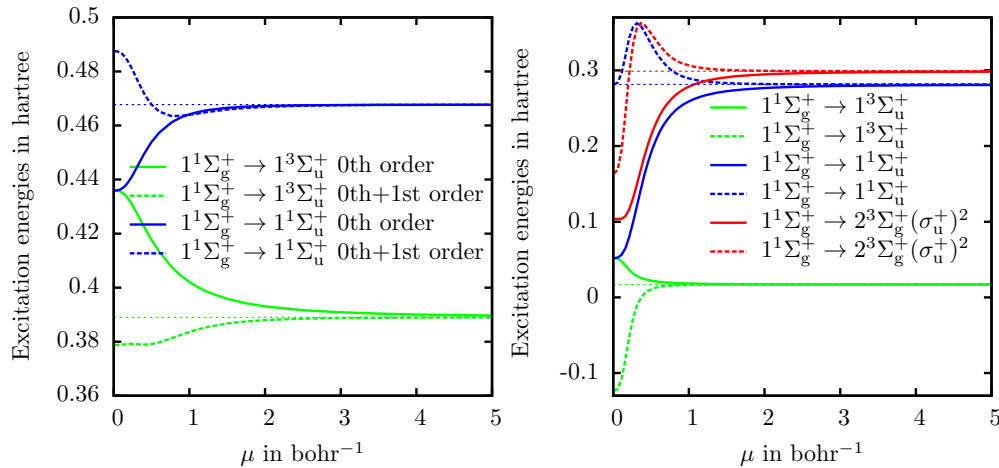
Figure 4.   Zeroth-order $\Delta\mathcal{E}_k^\mu$ (plain line) and zeroth+first-order $\Delta E_k^{\mu,(0+1)}$ (dashed line) excitation ener-
gies of the hydrogen molecule (in hartree) as a function of μ in bohr^{-1} at the equilibrium distance (left)
and three times the equilibrium distance (right). The excitation energies of the physical system ΔE_k are
plotted as horizontal dotted lines.

4.3.   *Hydrogen molecule*

In Figure 4, we have plotted the excitation energies of H_2 as a function of μ at the
equilibrium distance R_{eq} and at $3R_{\text{eq}}$. At the equilibrium geometry, the first-order
correction works well. At $\mu = 0$, the correction is in the right direction (singlet
and triplet excitation energies being raised and lowered, respectively); for nearly
all $\mu > 0$, the error is smaller than for the zeroth-order excitation energies.

Unfortunately, when the bond is stretched, this is no longer the case. At the
stretched geometry, the first excitation energy $1^1\Sigma_g^+ \to 1^3\Sigma_u^+$ becomes negative
for small values of μ and the error with respect to the physical excitation energy
is higher than in the zeroth-order case. Moreover, the ordering of the two singlet
excitation energies is incorrect at small μ and they exhibit strong oscillation when
the interaction is switched on. In this case, therefore, the zeroth-order excitation
energies are better approximations to the physical excitation energies.

5.   Conclusion

We have considered two variants of perturbation theory along a range-separated
adiabatic connection. The first and simpler variant, based on the usual Rayleigh–
Schrödinger perturbation theory, was tested on the helium and beryllium atoms and
on the hydrogen molecule at equilibrium and stretched geometries. Although total
energies are improved to first order in the perturbation, excitation energies are not
improved since the theory does not keep the density constant along the adiabatic
connection at each order of perturbation. It would be interesting to examine the
evolution of the ionization potential to understand better the effect of this variant
of the perturbation theory on our systems of interest.

The second variant of the perturbation theory, based on Görling–Levy theory,
should improve the results significantly by keeping the ground-state density con-
stant at each order in the perturbation [41], as already observed on the KS sys-
tem [45]. However, this more complicated theory has not yet been implemented for
$\mu > 0$.

An interesting alternative to perturbation theory is provided by extrapolation,
which make use of the behavior of the energies with respect to μ near the physical
system to estimate the exact energies from the energy of the partially interacting

system at a given μ and its first- or higher-order derivatives with respect to μ [72, 73]. Work using this approach will be presented elsewhere.

Acknowledgements

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Appendix A. Double adiabatic connection with a constant density

We here present a double adiabatic connection, depending on two parameters, that keeps the ground-state density constant. It is the basis for the perturbation theory presented in Section 2.2.2. A different density-fixed double adiabatic connection was considered in Refs. [74, 75].

The Levy–Lieb universal density functional for the Coulomb electron–electron

interaction $\hat{W}_{\text{ee}}$ is given by [76–78]

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle, \tag{A1}$$

We here generalize it to the interaction $\hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu}$, where $\hat{W}_{\text{ee}}^{\text{lr},\mu}$ and $\hat{W}_{\text{ee}}^{\text{sr},\mu}$ are long-range and short-range electron–electron interactions, respectively, that depend on both a range-separation parameter μ and on a linear parameter λ:

$$\begin{aligned}
F^{\mu,\lambda}[n] &= \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Psi \rangle \\
&= \langle \Psi^{\mu,\lambda}[n] | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Psi^{\mu,\lambda}[n] \rangle.
\end{aligned} \tag{A2}$$

The total universal density functional $F[n]$ is then decomposed into $F^{\mu,\lambda}[n]$ and a (μ,λ)-dependent short-range Hartree–exchange–correlation density functional $\bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n]$,

$$F[n] = F^{\mu,\lambda}[n] + \bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n], \tag{A3}$$

giving the following expression for the exact ground-state energy of the electronic system

$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n_\Psi] \right\}, \tag{A4}$$

where the minimization is over normalized multi-determinantal wave functions. The Euler–Lagrange equation corresponding to this minimization is

$$\hat{H}^{\mu,\lambda} | \Psi_0^{\mu,\lambda} \rangle = \mathcal{E}_0^{\mu,\lambda} | \Psi_0^{\mu,\lambda} \rangle, \tag{A5}$$

where $\Psi_0^{\mu,\lambda}$ and $\mathcal{E}_0^{\mu,\lambda}$ are the ground-state wave function and energy, respectively, of the Hamiltonian

$$\hat{H}^{\mu,\lambda} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} + \hat{\bar{V}}_{\text{Hxc}}^{\text{sr},\mu,\lambda}, \tag{A6}$$

where

$$\hat{\bar{V}}_{\text{Hxc}}^{\text{sr},\mu,\lambda} = \int \frac{\delta \bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n_0]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \, d\mathbf{r} \tag{A7}$$

is the short-range Hartree–exchange–correlation potential operator, evaluated at the ground-state density of the physical system at μ and λ, $n_0(\mathbf{r}) = \langle \Psi_0^{\mu,\lambda} | \hat{n}(\mathbf{r}) | \Psi_0^{\mu,\lambda} \rangle$. The Hamiltonian $\hat{H}^{\mu,\lambda}$ thus sets up a double adiabatic connection with a constant ground-state density.

The range-separated ground-state DFT formalism of Section 2.1 is recovered in the limit $\lambda = 0$. To set up a perturbation theory in λ about 0, we rewrite $\hat{H}^{\mu,\lambda}$ of Eq. (A6) as the sum of the noninteracting Hamiltonian $\hat{H}^{\text{lr},\mu} = \hat{H}^{\mu,\lambda=0}$ and a perturbation operator. For this purpose, the Hartree–correlation–exchange functional is written as

$$\bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n] = \bar{E}_{\text{Hxc}}^{\text{sr},\mu,\lambda=0}[n] - E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n], \tag{A8}$$

14

which defines the new functional $E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n]$. The Hamiltonian can now be rewritten as

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} - \hat{V}_{\text{Hxc}}^{\text{sr},\mu,\lambda}, \tag{A9}$$

where

$$\hat{V}_{\text{Hxc}}^{\text{sr},\mu,\lambda} = \int \frac{\delta E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n_0]}{\delta n(\mathbf{r})} \, \hat{n}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{A10}$$

is the short-range Hartree–exchange–correlation potential operator associated with $E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n]$.

The dependence on λ of $E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n]$ can be made more explicit. It is easy to show that

$$E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n] = \langle \Psi^{\mu,\lambda}[n] | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \lambda \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Psi^{\mu,\lambda}[n] \rangle$$
$$- \langle \Psi^{\mu,\lambda=0}[n] | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \Psi^{\mu,\lambda=0}[n] \rangle, \tag{A11}$$

which leads to the following decomposition

$$E_{\text{Hxc}}^{\text{sr},\mu,\lambda}[n] = \lambda E_{\text{Hx,md}}^{\text{sr},\mu}[n] + E_{\text{c,md}}^{\text{sr},\mu,\lambda}[n], \tag{A12}$$

where

$$E_{\text{Hx,md}}^{\text{sr},\mu}[n] = \langle \Psi^{\mu,\lambda=0}[n] | \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Psi^{\mu,\lambda=0}[n] \rangle \tag{A13}$$

is a multi-determinantal (md) generalization of the usual short-range Hartree–exchange functional [64–66]. Using the variational property of the wave function $\Psi^{\mu,\lambda}[n]$, and for non-degenerate wave functions $\Psi^{\mu,\lambda=0}[n]$, the expansion of $E_{\text{c,md}}^{\text{sr},\mu,\lambda}[n]$ in λ about 0 starts at second order:

$$E_{\text{c,md}}^{\text{sr},\mu,\lambda}[n] = \lambda^2 E_{\text{c,md}}^{\text{sr},\mu,(2)}[n] + \cdots, \tag{A14}$$

as in standard GL perturbation theory [40, 41]. The Hamiltonian of Eq. (A9) can now be rewritten as

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\text{lr},\mu} + \lambda \hat{W}^{\text{sr},\mu} - \hat{V}_{\text{c,md}}^{\text{sr},\mu,\lambda}, \tag{A15}$$

where the perturbation operator $\hat{W}^{\text{sr},\mu} = \hat{W}_{\text{ee}}^{\text{sr},\mu} - \hat{V}_{\text{Hx,md}}^{\text{sr},\mu}$ and

$$\hat{V}_{\text{Hx,md}}^{\text{sr},\mu} = \int \frac{\delta E_{\text{Hx,md}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{A16}$$

has been introduced to collect all the linear terms in λ, the remaining perturbation operator

$$\hat{V}_{\text{c,md}}^{\text{sr},\mu,\lambda} = \int \frac{\delta E_{\text{c,md}}^{\text{sr},\mu,\lambda}[n_0]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{A17}$$

containing all higher-order terms in λ.