

Excitation energies from density functional perturbation theory

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We consider two perturbative schemes to calculate excitation energies, each employing the Kohn–Sham Hamiltonian as the unperturbed system. Using accurate exchange–correlation potentials generated from essentially exact densities and their exchange components determined by a recently proposed method, we evaluate energy differences between the ground state and excited states in first-order perturbation theory for the helium, ionized lithium and beryllium atoms. It was recently observed that the zeroth-order excitation energies, simply given by the difference of the Kohn–Sham eigenvalues, almost always lie between the singlet and triplet experimental excitation energies, corrected for relativistic and finite nuclear mass effects. The first-order corrections provide about a factor of two improvement in one of the perturbative schemes but not in the other. The excitation energies within perturbation theory are found to be more accurate than the excitations obtained within Δ SCF while, for a two-electron system, they coincide with the ones obtained in time-dependent density functional theory within the single-pole approximation using our accurate static exchange–correlation potential and the time-dependent optimized effective potential kernel. We find that the agreement between the experimental and the perturbative excitation energies deteriorates significantly if potentials from approximate functionals such as the local density approximation and the optimized effective potential method are employed instead of the true Kohn–Sham potential. © 1997 American Institute of Physics. [S0021-9606(97)03147-4]

I. INTRODUCTION

Density functional theory is usually employed to study ground states. However, it is clear that density functional theory can in principle be used to calculate excitation energies since, according to the Hohenberg–Kohn theorem¹, the density determines the external potential (aside from an additive constant) and, consequently, the entire spectrum. In principle, one could construct functionals of the ground state densities that yield excitation energies.

There are several proposals in the literature to deal with excited states. Gunnarson and Lundquist² pointed out that the original Hohenberg–Kohn theorems can be generalized to apply to the lowest energy state of any given symmetry. Von Barth³ extended density functional theory to states of mixed symmetry following the observation of Ziegler *et al.*⁴ that the $X\alpha$ method is designed to describe states that have single determinant wave functions in the absence of interaction. The practical recipe consists of calculating, within the local density approximation, the energies of states of mixed symmetry represented by a single determinant and linearly combining them to construct the energies of the states of pure symmetry^{3–5}. Further developments and applications of this procedure, known as Δ SCF, can be found in Refs. 6–9. Another generalization of density functional theory to treat excited states is the ensemble density functional theory^{10–12}. Recently, a different and quite promising method to calculate

excited states based on time-dependent density functional theory has been developed^{13–17}.

An alternative approach¹⁸ is to calculate excitation energies perturbatively using the non-interacting Kohn–Sham Hamiltonian as the zeroth-order Hamiltonian. In the Kohn–Sham formulation of density functional theory¹⁹, the interacting electron system is replaced by a system of non-interacting electrons in an effective local potential that yields the true ground state density. In the perturbative approach, the zeroth-order excitation energies are simply the differences of Kohn–Sham eigenvalues. Remarkably, it has been recently shown²⁰ that, for atomic systems, the excitation energies obtained as differences of Kohn–Sham eigenvalues lie between the triplet and singlet experimental excitation energies, corrected for relativistic and finite nuclear mass effects, with the exception of the $1s \rightarrow 3d$ transition of ionized lithium. This finding is surprising since, except for the highest occupied orbital, there is no strict relationship between the Kohn–Sham eigenvalues and excitation energies.

In an attempt to improve on these results and determine the singlet–triplet splitting, we calculate excitation energies to first order in perturbation theory. We employ two variants of perturbation theory. Interestingly, we find that the first-order corrections from the more obvious *standard perturbation theory* make the excitation energies worse on average while those from the *coupling-constant perturbation theory*

of Görling and Levy²¹ yield about a factor of two improvement. To perform these calculations, we employ excellent approximations to the true Kohn–Sham exchange–correlation potentials determined by generating an accurate density for the system of interest and then computing an exchange–correlation potential that yields the desired density as the ground state solution for the fictitious non-interacting system^{22–24}. Evaluating the first-order corrections also requires the knowledge of the correct exchange component of the exchange–correlation potential as determined in our previous work²⁵. Standard perturbation theory has also been recently applied to calculate ground state energies and the perturbation series based on various approximate exchange–correlation functionals were found to be divergent for the systems tested²⁶.

In Sec. II A, we briefly introduce the Kohn–Sham formulation of density functional theory. In Sec. II B, we present the coupling-constant scheme and the formulae used to determine the excitation energies to first order in the coupling constant. In Sec. III, we give the results and a comparison with other methods to evaluate excitation energies. The perturbation theory scheme is also implemented using approximate exchange–correlation functionals. In the Appendix, we derive the formulae for the first-order corrections to the excitation energies.

II. THEORETICAL BACKGROUND

A. Kohn–Sham method

In the Kohn–Sham formulation of density functional theory¹⁹, the ground state density is written in terms of single-particle orbitals obeying the equations in atomic units ($\hbar = e = m = 1$):

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}([\rho]; \mathbf{r}) \right\} \psi_i = \epsilon_i \psi_i, \quad (1)$$

where

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2)$$

The electronic density is constructed by summing over the N lowest energy orbitals where N is the number of electrons. $v_{\text{ext}}(\mathbf{r})$ is the external potential and $v_{\text{H}}(\mathbf{r})$ the Hartree potential. The exchange–correlation potential $v_{\text{xc}}([\rho]; \mathbf{r})$ is written as the sum of two separate contributions for exchange and correlation, $v_{\text{xc}}([\rho]; \mathbf{r}) = v_{\text{x}}([\rho]; \mathbf{r}) + v_{\text{c}}([\rho]; \mathbf{r})$.

B. Perturbation theory

In many-body perturbation theory the Hamiltonian \mathcal{H} is written as the sum of a zeroth-order Hamiltonian \mathcal{H}_0 and a perturbing Hamiltonian $\mathcal{H}_1 = \mathcal{H} - \mathcal{H}_0$.

In the commonly used Möller–Plesset perturbation theory²⁷, the zeroth-order Hamiltonian is the Fock operator:

$$\mathcal{H}_0^{\text{HF}} = T + V_{\text{ext}} + V_{\text{H}} + V_{\text{x}}^{\text{HF}}, \quad (3)$$

while in density functional perturbation theory

$$\mathcal{H}_0 = T + V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}}, \quad (4)$$

where T is the kinetic operator and V_{x}^{HF} is the non-local Hartree–Fock exchange operator. Here and elsewhere, we employ the notation that potentials are capitalized when summed over all the electrons. The perturbation corresponding to the zeroth-order (Eq. 4) is clearly given by

$$\mathcal{H}_1 = V_{\text{ee}} - V_{\text{H}} - V_{\text{xc}}. \quad (5)$$

The other variant of perturbation theory we consider is due to Görling and Levy²¹ and is based on the adiabatic connection Hamiltonian which links the Kohn–Sham Hamiltonian with the fully interacting Hamiltonian keeping the ground state density constant independent of α :

$$\mathcal{H}^\alpha = T + V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}} + \alpha(V_{\text{ee}} - V_{\text{x}} - V_{\text{H}}) - V_{\text{c}}^\alpha. \quad (6)$$

v_{c}^α is second order in α ²¹ and equals the correlation potential when $\alpha=1$. The zeroth-order Hamiltonian is again the Kohn–Sham Hamiltonian and the perturbing Hamiltonian contains a term

$$\mathcal{H}_1^{(1)} = \alpha(V_{\text{ee}} - V_{\text{H}} - V_{\text{x}}), \quad (7)$$

which is linear in the perturbation parameter α and a component $-v_{\text{c}}^\alpha$ which contains second and higher order contributions²¹. To any order in perturbation theory, the density equals the true ground state density to that order in the coupling constant²¹.

Let us consider the excitation of an electron from the space-spin orbital ϕ_k to ϕ_ν . In both perturbative schemes, the zeroth-order energy difference equals the difference in the expectation value of the Kohn–Sham Hamiltonian on the eigenstates Φ and $\Phi_{k\nu}$, obtained from Φ by exciting an electron from orbital k to orbital ν , and is simply the difference of the Kohn–Sham eigenvalues:

$$\Delta E^{(0)} = \epsilon_\nu - \epsilon_k. \quad (8)$$

The correction to first order in the coupling constant (Eq. 7) is given by

$$\Delta E^{(1)} = \langle \Phi_{k\nu} | V_{\text{ee}} - V_{\text{H}} - V_{\text{x}} | \Phi_{k\nu} \rangle - \langle \Phi | V_{\text{ee}} - V_{\text{H}} - V_{\text{x}} | \Phi \rangle. \quad (9)$$

This expression simplifies for the helium, ionized lithium and beryllium atoms, that we use as examples in this work, all having ground states of ¹S symmetry. The excited states are either singlets or triplets. Let Φ_0 be the Kohn–Sham ground state and $\Phi_{k\nu}$ the excited state obtained by exciting an electron from a (doubly occupied) orbital k to orbital ν . In this case, as shown in Ref. 18 and the Appendix, the first-order energy difference between the ground state and the state $\Phi_{k\nu}$ depends on whether $\Phi_{k\nu}$ is a triplet or a singlet and is given respectively by

$$\begin{aligned} \Delta E^{(1)}(T, k \rightarrow \nu) = & \langle \phi_\nu | \hat{v}_{\text{x}}^{\text{HF}} - v_{\text{x}} | \phi_\nu \rangle - \langle \phi_k | \hat{v}_{\text{x}}^{\text{HF}} - v_{\text{x}} | \phi_k \rangle \\ & - \langle \psi_\nu \psi_k | g | \psi_\nu \psi_k \rangle, \end{aligned} \quad (10)$$

and

$$\Delta E^{(1)}(S, k \rightarrow \nu) = \langle \phi_\nu | \hat{v}_x^{\text{HF}} - v_x | \phi_\nu \rangle - \langle \phi_k | \hat{v}_x^{\text{HF}} - v_x | \phi_k \rangle - \langle \psi_\nu \psi_k | g | \psi_\nu \psi_k \rangle + 2 \langle \psi_\nu \psi_k | g | \psi_k \psi_\nu \rangle, \quad (11)$$

where $g = 1/|\mathbf{r} - \mathbf{r}'|$ and ψ is just the spatial component of the orbital ϕ . \hat{v}_x^{HF} is the Hartree–Fock exchange potential, but constructed from the Kohn–Sham orbitals occupied in ground state Φ_0 .

To evaluate the correction within the standard perturbation theory (Eq. 5), we simply replace v_x with v_{xc} in the above formulae.

III. RESULTS AND DISCUSSION

In order to evaluate the excitation energies to first order in the coupling constant (Eqs. 8, 10 and 11) and in the more standard perturbation scheme, we need to determine an accurate exchange–correlation potential, Kohn–Sham orbitals and eigenvalues and the exchange component of the exchange–correlation potential for the system of interest.

As mentioned in Sec. I, the accurate exchange–correlation potential used in Eq. 1 for the determination of the Kohn–Sham orbitals and eigenvalues is obtained starting from an accurate density and searching for a potential that yields the desired density as a solution of the Kohn–Sham equations (Eqs. 1 and 2). In the special case of the singlet ground state of a two-electron system,^{28,29} the exchange–correlation potential can be simply obtained from Eq. 1. For systems with more than two electrons, v_{xc} can be determined by expanding it in a complete set of basis functions and varying the expansion coefficients such that Eqs. 1 and 2 yield the accurate density.^{22–24} The exchange component of the exchange–correlation potential is simply given by the condition that it cancels the self-interaction term in the Hartree potential in the case of two electrons in the singlet ground state. For a many-electron system, the exchange potential is obtained as discussed in Ref. 25.

A. Exact perturbative excitation energies

In Fig. 1 and in Tables I, II and III, we show the excitation energies to zeroth order and to first order in the two perturbative schemes for helium, ionized lithium and beryllium respectively.

The zeroth-order excitation energies are simply given by the difference in the Kohn–Sham eigenvalues and, as already discussed in Ref. 20, lie between the experimental triplet and singlet excitation energies to an accuracy of four significant digits, provided that relativistic and finite nuclear mass effects are taken into account. The only exception is the $1s \rightarrow 3d$ transition for ionized lithium.

The first-order excitation energies obtained from standard perturbation theory are on average less accurate than the zeroth-order energies. In contrast, the excitation energies to first order in the coupling constant are on average better than the zeroth-order energies but the improvement is not consistently present for all the excitations. With the exception of the $2s$ to $3d$, $4p$ and $4d$ excitations for beryllium, the singlet–triplet splittings, obtained from either first-order

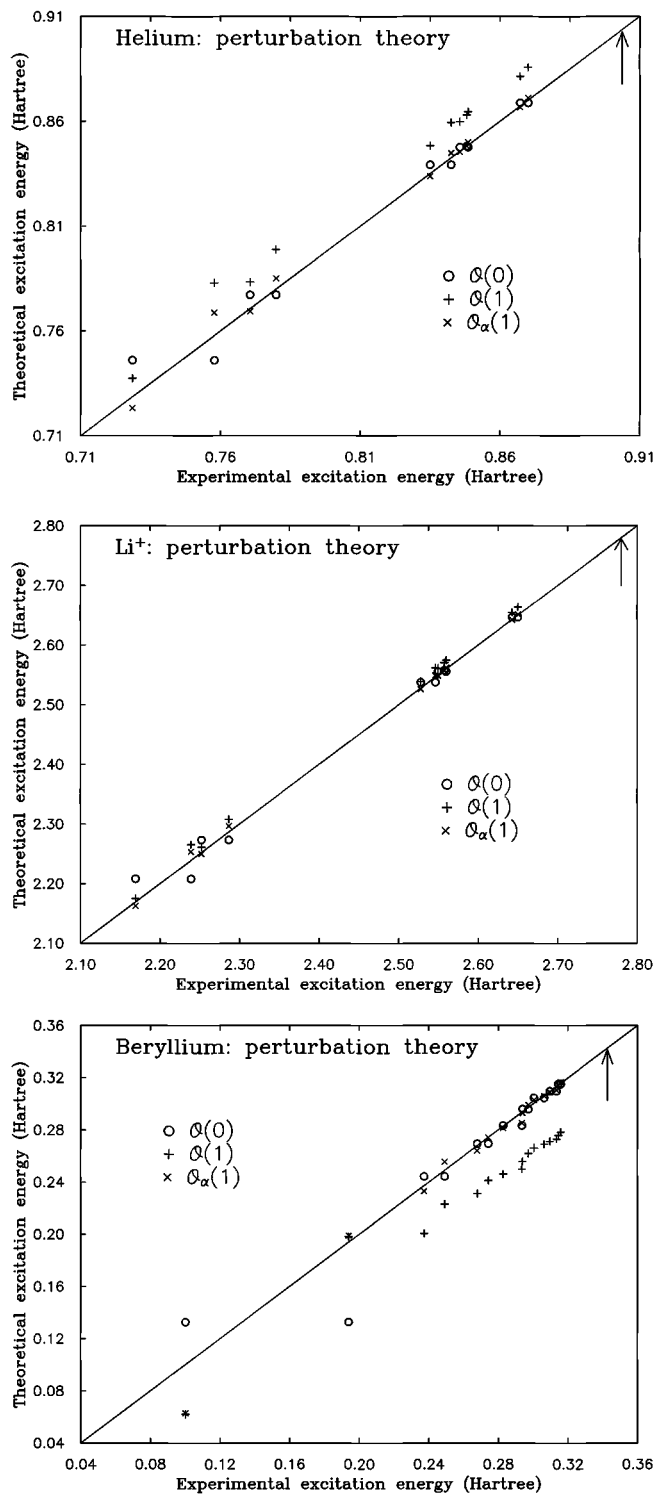


FIG. 1. Theoretical versus experimental excitation energies for He, Li^+ and Be (see Tables I–III). $\mathcal{O}(0)$ is the zeroth-order perturbative result. $\mathcal{O}(1)$ and $\mathcal{O}_\alpha(1)$ are the first-order results in the standard and in coupling-constant perturbation schemes respectively. The ionization limits are indicated by arrows.

scheme, are too large. Note that for the two-electron systems, as shown in the Appendix, Eqs. 10 and 11 yield a symmetrical splitting around the zeroth-order excitation energy.

From Fig. 1, it is clear that the theoretical predictions for

TABLE I. Excitation energies of He in hartree atomic units. The theoretical energies of Drake (Ref. 34) and the perturbative results are for infinite nuclear mass and neglect relativity. $\mathcal{O}(0)$ is the zeroth-order perturbative result. $\mathcal{O}(1)$ and $\mathcal{O}_\alpha(1)$ are the first-order results in the standard and in coupling-constant perturbation schemes respectively.

Transition	Final state	Experiment	Drake	$\mathcal{O}(0)$	$\mathcal{O}(1)$	$\mathcal{O}_\alpha(1)$
$1s \rightarrow 2s$	$2\ ^3S$	0.7283	0.7285		0.7374	0.7232
	$2\ ^1S$	0.7576	0.7578	0.7460	0.7829	0.7687
$1s \rightarrow 2p$	$1\ ^3P_o$	0.7704	0.7706		0.7833	0.7693
	$1\ ^1P_o$	0.7797	0.7799	0.7772	0.7989	0.7850
$1s \rightarrow 3s$	$3\ ^3S$	0.8349	0.8350		0.8483	0.8337
	$3\ ^1S$	0.8423	0.8425	0.8392	0.8594	0.8448
$1s \rightarrow 3p$	$2\ ^3P_o$	0.8455	0.8456		0.8598	0.8453
	$2\ ^1P_o$	0.8484	0.8486	0.8476	0.8645	0.8500
$1s \rightarrow 3d$	$1\ ^3D$	0.8479	0.8481		0.8629	0.8481
	$1\ ^1D$	0.8479	0.8481	0.8481	0.8630	0.8482
$1s \rightarrow 4s$	$4\ ^3S$	0.8670	0.8672		0.8814	0.8667
	$4\ ^1S$	0.8700	0.8701	0.8688	0.8857	0.8710

the higher excitation energies converge to the experimental excitation energies both in zeroth-order and in first-order coupling constant perturbation theory. On the other hand, the excitation energies from first-order standard perturbation theory converge to a too large value for helium and ionized lithium and a too low value for beryllium. It is apparent that the zeroth-order energies must converge to the experimental energies since the highest occupied Kohn–Sham eigenvalue is the negative of the ionization energy³⁰. In Fig. 1, the ionization limit for each system has been indicated by an arrow. There is an explanation of why the higher excitation energies from first-order coupling constant perturbation theory con-

verge to the experimental excitation energies³¹. Coupling constant perturbation theory is based on the coupling constant Hamiltonian in which the external potential is varied to keep the charge density constant for all values of the coupling constant α . Since the ionization energy is related to the asymptotic decay of the charge density, it is independent of the coupling constant. Now, let us consider a perturbation expansion of the ionization energy and charge density in powers of the coupling constant. Since the ionization energy and density are independent of the coupling constant, each term in the series, except the zeroth-order term, must be zero. If we perform perturbation theory to a finite order, the ion-

TABLE II. Excitation energies of Li^+ in hartree atomic units. The theoretical energies of Drake (Ref. 35) and the perturbative results are for infinite nuclear mass and neglect relativity. $\mathcal{O}(0)$ is the zeroth-order perturbative result. $\mathcal{O}(1)$ and $\mathcal{O}_\alpha(1)$ are the first-order results in the standard and in coupling-constant perturbation schemes respectively.

Transition	Final state	Experiment	Drake	$\mathcal{O}(0)$	$\mathcal{O}(1)$	$\mathcal{O}_\alpha(1)$
$1s \rightarrow 2s$	$2\ ^3S$	2.1690	2.1692		2.1748	2.1628
	$2\ ^1S$	2.2330	2.2390	2.2082	2.2655	2.2535
$1s \rightarrow 2p$	$1\ ^3P_o$	2.2521	2.2522		2.2612	2.2499
	$1\ ^1P_o$	2.2865	2.2866	2.2733	2.3079	2.2966
$1s \rightarrow 3s$	$3\ ^3S$	2.5277	2.5278		2.5387	2.5261
	$3\ ^1S$	2.5460	2.5462	2.5375	2.5615	2.5489
$1s \rightarrow 3p$	$2\ ^3P_o$	2.5493	2.5495		2.5611	2.5487
	$2\ ^1P_o$	2.5595	2.5597	2.5554	2.5745	2.5621
$1s \rightarrow 3d$	$1\ ^3D$	2.5572	2.5574		2.5702	2.5574
	$1\ ^1D$	2.5574	2.5575	2.5576	2.5706	2.5578
$1s \rightarrow 4s$	$4\ ^3S$	2.6426	2.6428		2.6548	2.6421
	$4\ ^1S$	2.6499	2.6501	2.6466	2.6638	2.6511

TABLE III. Excitation energies of Be in hartree atomic units. The perturbative results are for infinite nuclear mass and neglect relativity. $\mathcal{E}(0)$ is the zeroth-order perturbative result. $\mathcal{E}(1)$ and $\mathcal{E}_\alpha(1)$ are the first-order results in the standard and in coupling-constant perturbation schemes respectively.

Transition	Final state	Experiment	$\mathcal{E}(0)$	$\mathcal{E}(1)$	$\mathcal{E}_\alpha(1)$
$2s \rightarrow 2p$	$1\ ^3P_o$	0.1002		0.0621	0.0629
	$1\ ^1P_o$	0.1939	0.1327	0.1981	0.1989
$2s \rightarrow 3s$	$2\ ^3S$	0.2373	0.2444	0.2006	0.2331
	$2\ ^1S$	0.2491		0.2231	0.2556
$2s \rightarrow 3p$	$2\ ^3P_o$	0.2679	0.2694	0.2311	0.2640
	$2\ ^1P_o$	0.2742		0.2412	0.2741
$2s \rightarrow 3d$	$1\ ^3D$	0.2827	0.2833	0.2460	0.2814
	$1\ ^1D$	0.2936		0.2498	0.2852
$2s \rightarrow 4s$	$3\ ^3S$	0.2939	0.2959	0.2557	0.2928
	$3\ ^1S$	0.2973		0.2619	0.2990
$2s \rightarrow 4p$	$3\ ^3P_o$	0.3005	0.3046	0.2660	0.3029
	$3\ ^1P_o$	0.3063		0.2691	0.3061
$2s \rightarrow 4d$	$2\ ^3D$	0.3096	0.3098	0.2713	0.3089
	$2\ ^1D$	0.3134		0.2730	0.3106
$2s \rightarrow 5s$	$4\ ^3S$	0.3144	0.3153	0.2758	0.3139
	$4\ ^1S$	0.3156		0.2784	0.3166

ization energy is still strictly constant at each order: Since the ionization energy is obtained as an energy difference, each order of perturbation theory contributes only to that same order. We note in passing that this is not true of the density. At a given order of perturbation theory, the density is correct only to that order since the n -th order wave function gives an $(n+1)$ -th order contribution to the charge density that is canceled only by going to the $(n+1)$ -th order of perturbation theory. Finally, we note that the reason why the first-order energies in the standard perturbation theory are too high for helium and ionized lithium and too low for beryllium is that the correlation potential, v_c , is mostly positive for the former and entirely negative for the latter²⁴. As explained in Sec. II B, the first-order excitation energies in standard perturbation theory differ from the energies to first order in the coupling constant in having v_{xc} instead of only v_c in Eqs. 10 and 11.

We observe from Fig. 1 that the zeroth order and first order in coupling constant results are accurate not only close to the ionization limit but over most of the energy range. This calls for some further explanation beyond that provided above. In Ref. 20 the accuracy of the zeroth-order excitation energies is attributed to the additional fact that the Kohn–Sham orbitals and the quasi-particle amplitudes satisfy the same equation to order $1/r^4$.

We wish to emphasize that the accuracy of the first-order excitation energies, obtained as differences of first-order total energies of the ground and excited states, does not extend to the individual total energies of the ground and excited states.

TABLE IV. Root mean square errors of the excitation energies of He, Li⁺ and Be in zeroth-order and first-order perturbation theory.

System	$\mathcal{E}(0)$	$\mathcal{E}(1)$	$\mathcal{E}_\alpha(1)$
He	0.0067	0.0159	0.0039
Li ⁺	0.0167	0.0148	0.0056
Be	0.0178	0.0358	0.0099

From Eq. 5, we obtain for the ground state energy to first order in the coupling constant:

$$E^{(1)} = \langle \Phi_0 | \mathcal{H}^{(0)} + \mathcal{H}^{(1)} | \Phi_0 \rangle \\ = \langle \Phi_0 | T + V_{\text{ext}} + V_{\text{ee}} + V_c | \Phi_0 \rangle. \quad (12)$$

Now, $\langle \Phi_0 | T + V_{\text{ext}} + V_{\text{ee}} | \Phi_0 \rangle$ yields an energy that is a little worse than the energy from either the optimized effective potential (OEP) method³² or the Hartree–Fock method since the Hartree–Fock wave function is the best single-determinant wave function, while $\langle \Phi_0 | V_c | \Phi_0 \rangle$ can be either negative or positive. For example, it is negative for beryllium but positive for helium, ionized lithium and neon. Consequently, at least for some systems, the ground state energies obtained from the first-order formula are worse than those from Hartree–Fock and the typical errors in Hartree–Fock total energies are considerably larger than the errors we obtain for the perturbative excitation energies.

We summarize the results in Table IV, which shows the root mean square errors in the excitation energies for our three test systems in zeroth-order and first-order perturbation theory. For the perturbation in the coupling constant, the errors are reduced by about a factor of two for helium and beryllium and a factor of three for ionized lithium. For the standard perturbation theory, the errors are about a factor of two worse than in zeroth order for helium and beryllium while a slight improvement is obtained for ionized lithium.

In addition to the excitations from the highest occupied level that we have considered so far, we also studied the core-level excitation of beryllium from the $1s$ orbital to the $2p$ orbital, $1s^2 2s^2 1S \rightarrow 1s^1 2s^2 2p^1 1P$. The experimental energy is 4.243 hartree³³, while the zeroth-order perturbative energy is 4.017 hartree and the first-order perturbative energies for the 3P and 1P states are 4.440 and 4.460 hartree respectively. Clearly, neither the zeroth-order nor the first-order energies agree with experiment as closely as do the energies of excitations from the highest occupied level. This is related to the fact that the eigenvalues of the occupied orbitals, other than the highest, are not strictly related to the corresponding ionization energies.

B. Approximate excitation energies within perturbation theory and other schemes

Just as Møller–Plesset perturbation theory is commonly used in quantum chemistry calculations, density functional perturbation theory could become a feasible technique to access excited states. However, the results presented above were obtained using the true Kohn–Sham potentials whereas practical implementations of the method would need to use

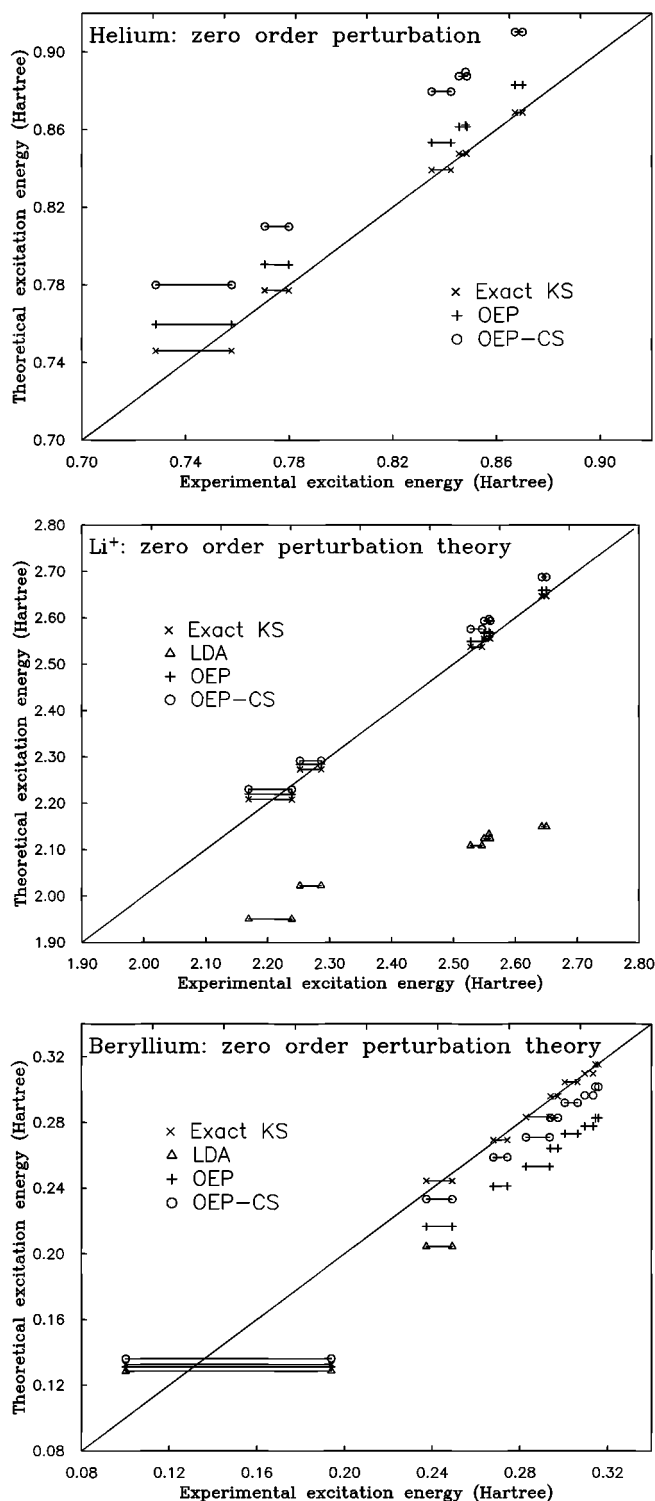


FIG. 2. Zeroth-order perturbation theory excitation energies for He, Li^+ and Be. The theoretical excitation energies obtained from the exact Kohn–Sham, LDA, OEP and OEP–Colle–Salvetti eigenvalues are plotted versus the experimental values. The singlet and triplet energies from the same configuration are joined by lines.

potentials obtained from approximate exchange–correlation functionals. In Fig. 2, we compare the zeroth-order excitation energies obtained from the local density approximation (LDA) and the optimized effective potential method with

those obtained from the true Kohn–Sham potential. The LDA does not bind any of the unoccupied orbitals in helium and binds only the lowest two unoccupied orbitals in beryllium. Hence, the sparsity of LDA data in Fig. 2. Since the highest occupied level in LDA is always too shallow, the zeroth-order LDA excitation energies are on average too small. However, note that the lowest excitation energies of beryllium from all three potentials are very close. The reason is that this excitation is within the same principal quantum number shell ($2s \rightarrow 2p$) and, consequently, both orbitals involved in the excitation explore the same, rather limited, spatial region. The OEP excitation energies are too high for helium and ionized lithium and too low for beryllium, which of course is due to the correlation potential being predominantly positive for the former and negative for the latter²⁴.

In Fig. 3, we present the same comparisons for the excitation energies obtained within first-order coupling-constant perturbation theory. The first-order OEP and first-order exact Kohn–Sham energies split in a roughly symmetrical way about the corresponding zeroth-order values while the first-order LDA energies have a large positive shift relative to the LDA zeroth order. The reason is the following. The second term in Eqs. 10 and 11, $-\langle \phi_k | \hat{v}_x^{\text{HF}} - v_x | \phi_k \rangle$, is strictly zero for both the true Kohn–Sham potential³⁶ and for the OEP potential³⁷ when ϕ_k is the highest occupied level. On the other hand, this identity does not hold for the LDA exchange potential which is in fact considerably shallower than the true one, resulting in a large positive contribution from this term. Note that all three quantities, ϕ_k , \hat{v}_x^{HF} and v_x , depend on whether they are being calculated for the true Kohn–Sham theory, OEP or LDA but the main difference comes from the change in v_x .

We do not show generalized gradient approximation (GGA) results in Figs. 2 and 3 but we find that the existing GGAs do not yield a large improvement upon the LDA results. This is to be expected since the GGA potentials also fail to have the correct asymptotic decay at large distances and are too shallow for much of the region where the charge density is appreciable.

Recently, there has been considerable interest in using time-dependent density functional theory (TDFT) to calculate excitation energies. In performing these calculations, a choice has to be made for the static potential and for the dynamic response. In Fig. 4, we compare the TDFT excitation energies of helium, obtained by Petersilka, Gossman and Gross¹⁷ using our exact Kohn–Sham potential and the dynamic response from OEP, to our first-order coupling-constant perturbation theory results. The agreement is very close and on the scale of the plot the difference between the two theories can only be detected for the lowest two excitations. For two-electron systems, it is indeed possible to show that the TDFT excitation energies obtained within the single-pole approximation, using the exact Kohn–Sham potential and the time-dependent OEP kernel, are strictly identical to the excitation energies derived in first-order perturbation theory in the coupling constant (Eqs. 10 and 11). The fact that, in this case, the single-pole approximation gives the

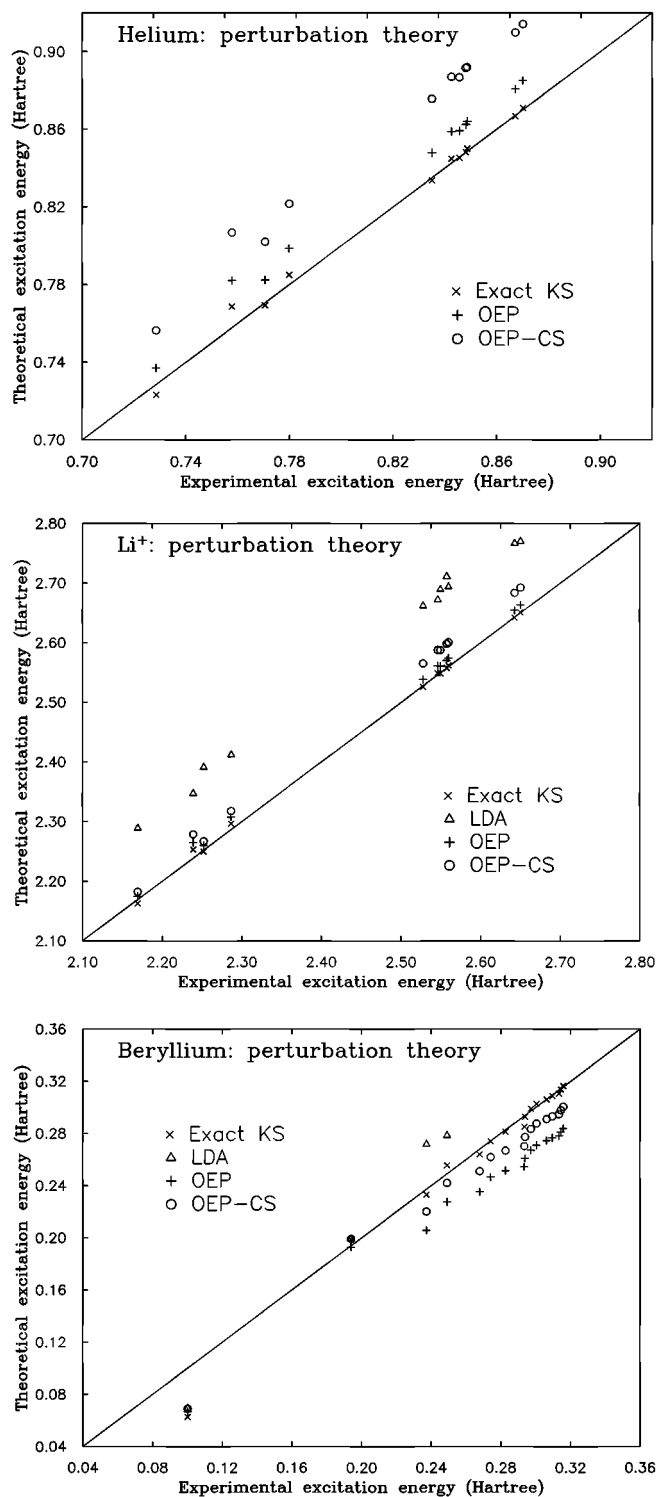


FIG. 3. Excitation energies for He, Li^+ and Be to first-order perturbation theory in the coupling constant. The theoretical excitation energies obtained from the exact Kohn–Sham solutions, LDA, OEP and OEP-Colle–Salvetti are plotted versus the experimental values.

leading correction to the Kohn–Sham eigenvalue differences¹⁷ explains the close agreement found in Fig. 4.

As mentioned in the Introduction, an older method for calculating excitation energies is the ΔSCF method^{3,4}. Relative to perturbation theory, ΔSCF has the advantage that,

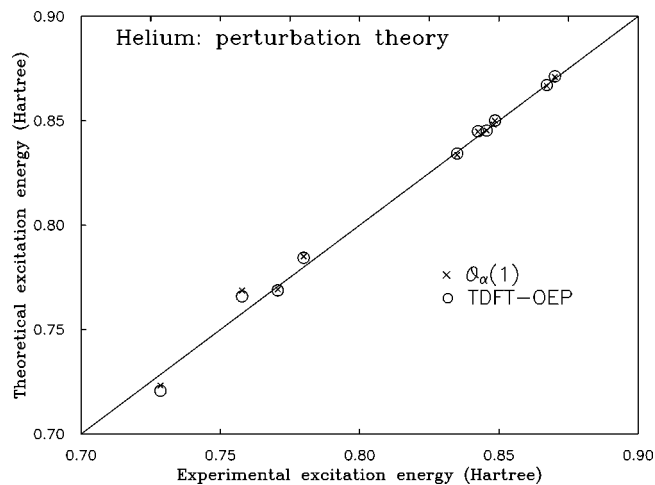


FIG. 4. Excitation energies for He within first-order perturbation theory in the coupling constant and time-dependent density functional theory. The time-dependent DFT excitation energies are obtained (Ref. 17) using the exact Kohn–Sham potential as static potential and OEP for the dynamical response. The theoretical excitation energies are plotted versus the experimental values.

when using approximate functionals, it can be applied even when the corresponding approximate exchange–correlation potential does not bind any unoccupied orbital. In Fig. 5, we compare the excitation energies of beryllium from ΔSCF , using the LDA potential. The results obtained for beryllium are somewhat more accurate than those from perturbation theory using the LDA or OEP potentials but of course are not as good as the perturbation theory results using the true Kohn–Sham potential. Also for ionized lithium, we find that, although less accurate than the perturbation results with the exact Kohn–Sham solutions, the ΔSCF energies are more accurate than the LDA perturbative energies and of comparable accuracy to the perturbative OEP results.

One can ask if it is possible to improve upon the perturbation theory results obtained with the exact exchange (OEP) functional by adding an approximate correlation functional.

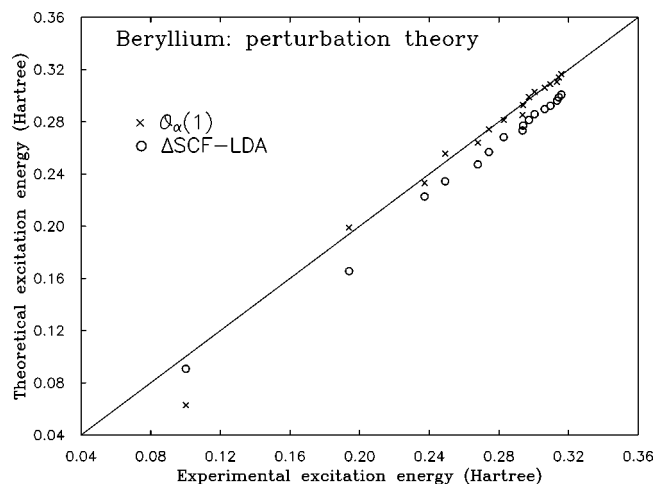


FIG. 5. Excitation energies for Be within first-order perturbation theory in the coupling constant and $\Delta\text{SCF-LDA}$. The theoretical excitation energies are plotted versus the experimental values.

Unfortunately, the correlation potentials obtained from the LDA and various GGA correlation functionals bear no resemblance to the true correlation potential²⁴. Recently, there has been considerable interest³⁸ in orbital-dependent correlation functionals, the most popular one being the Colle–Salvetti functional³⁹. In Figs. 1 and 2, we also show the correlation energies obtained from adding the Colle–Salvetti correlation functional to the true exchange (OEP) functional. The energies are improved for beryllium but are worse for helium and ionized lithium since the Colle–Salvetti correlation potential is mostly negative for all three systems whereas the true correlation potential is negative for beryllium but mostly positive for helium and ionized lithium.

Clearly, a present obstacle to the success of perturbation theory in the coupling constant seems to be the lack of an accurate approximation for the exchange-correlation functional. Since approximate functionals such as the local density or generalized gradient approximations bind few (if any) unoccupied orbitals, combining an exact treatment of exchange with a local orbital-dependent correlation functional, better than the Colle–Salvetti functional, appears to be the most promising possibility in this direction.

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APPENDIX: FIRST-ORDER CORRECTION

We obtain here the expressions for the first-order energy differences given in Eqs. 10 and 11. We consider the ground state Kohn–Sham determinant Φ_0 and an excited determinant $\Phi_{k\nu}$ obtained by exciting an electron from a doubly occupied orbital k to an empty orbital ν .

First, we rewrite the contributions to the first-order energy difference (Eq. 9) in terms of the Kohn–Sham orbitals:

$$\langle \Phi_{k\nu} | v_H + v_x | \Phi_{k\nu} \rangle - \langle \Phi_0 | v_H + v_x | \Phi_0 \rangle = \langle \phi_\nu | v_H + v_x | \phi_\nu \rangle - \langle \phi_k | v_H + v_x | \phi_k \rangle, \quad (\text{A1})$$

and

$$\langle \Phi | V_{\text{ee}} | \Phi \rangle = \frac{1}{2} \sum_{i,j}^{\text{occ}} (\langle ij | g | ij \rangle - \langle ij | g | ji \rangle),$$

where $\langle ij | g | rs \rangle \equiv \langle \phi_i \phi_j | g | \phi_r \phi_s \rangle = \iint d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') g \phi_r(\mathbf{r}) \phi_s(\mathbf{r}')$ and the sum is over the orbitals occupied in

the determinant Φ . Since the Hartree potential v_H is constructed from the orbitals occupied in the ground state Φ_0 , we obtain

$$\begin{aligned} & \langle \Phi_{k\nu} | V_{\text{ee}} | \Phi_{k\nu} \rangle - \langle \Phi_0 | V_{\text{ee}} | \Phi_0 \rangle \\ &= \sum_j^{\text{occ}} (-\langle kj | g | kj \rangle + \langle kj | g | jk \rangle \\ & \quad + \langle \nu j | g | \nu j \rangle - \langle \nu j | g | j \nu \rangle) - \langle \nu k | g | \nu k \rangle + \langle \nu k | g | k \nu \rangle \\ &= -\langle k | v_H + \hat{v}_x^{\text{HF}} | k \rangle + \langle \nu | v_H + \hat{v}_x^{\text{HF}} | \nu \rangle - \langle \nu k | g | \nu k \rangle \\ & \quad + \langle \nu k | g | k \nu \rangle, \end{aligned} \quad (\text{A2})$$

where the sums are over the Kohn–Sham orbitals occupied in Φ_0 and \hat{v}_x^{HF} is the Hartree–Fock exchange potential constructed from these orbitals. Combining Eqs. 9, A1, A2, we obtain

$$\begin{aligned} \Delta E^{(1)} &= \langle \phi_\nu | \hat{v}_x^{\text{HF}} - v_x | \phi_\nu \rangle - \langle \phi_k | \hat{v}_x^{\text{HF}} - v_x | \phi_k \rangle \\ & \quad - \langle \phi_\nu \phi_k | g | \phi_\nu \phi_k \rangle + \langle \phi_\nu \phi_k | g | \phi_k \phi_\nu \rangle. \end{aligned} \quad (\text{A3})$$

Our derivation of Eq. A3 is for a single-determinant $\Phi_{k\nu}$. If the final state is a triplet, its Kohn–Sham wave function can be written in terms of a single determinant provided that we consider either the $S_z = 1$ or the $S_z = -1$ components of the triplet. Then, the third term is zero since we are considering the excitation from $\phi_k = \psi_k \chi_\downarrow$ to $\phi_\nu = \psi_\nu \chi_\uparrow$ or from $\phi_k = \psi_k \chi_\uparrow$ to $\phi_\nu = \psi_\nu \chi_\downarrow$. If $\Phi_{k\nu}$ is a singlet, it is necessary to write $\Phi_{k\nu}$ as a sum of two determinants. There are two possible excitations, $\psi_k \chi_\uparrow \rightarrow \psi_\nu \chi_\uparrow$ and $\psi_k \chi_\downarrow \rightarrow \psi_\nu \chi_\downarrow$, and the resulting wave function is equal to $\Phi_{k\nu} = (\Phi_1 - \Phi_2) / \sqrt{2}$. Consequently,

$$\begin{aligned} \langle \Phi_{k\nu} | V_{\text{ee}} | \Phi_{k\nu} \rangle &= \frac{1}{2} [\langle \Phi_1 | V_{\text{ee}} | \Phi_1 \rangle + \langle \Phi_2 | V_{\text{ee}} | \Phi_2 \rangle \\ & \quad - \langle \Phi_1 | V_{\text{ee}} | \Phi_2 \rangle - \langle \Phi_2 | V_{\text{ee}} | \Phi_1 \rangle]. \end{aligned}$$

The first and second contribution are equal to each other and equivalent to the above calculation A3. The last two contributions are equal and, if we define $\phi_1 = \psi_k \chi_\downarrow$, $\phi_2 = \psi_\nu \chi_\uparrow$, $\phi_3 = \psi_k \chi_\uparrow$ and $\phi_4 = \psi_\nu \chi_\downarrow$, give

$$\begin{aligned} & -\frac{1}{2} [\langle \Phi_1 | V_{\text{ee}} | \Phi_2 \rangle + \langle \Phi_2 | V_{\text{ee}} | \Phi_1 \rangle] \\ &= -\langle \phi_1 \phi_2 | g | \phi_3 \phi_4 \rangle + \langle \phi_1 \phi_2 | g | \phi_4 \phi_3 \rangle. \end{aligned}$$

The first term is zero due to spin orthogonality while the second term can be rewritten as $\langle \psi_k \psi_\nu | g | \psi_\nu \psi_k \rangle$. Combining the above results, we obtain Eqs. 10 and 11.

In Sec. II B, we mentioned that, for two electrons in a singlet state, formulae (Eqs. 10 and 11) yield a symmetrical splitting around the zeroth-order excitation energy. The ground state Kohn–Sham determinant of two electrons in a singlet state is constructed from the two orbitals $\phi_1 = \psi_0 \chi_\uparrow$ and $\phi_2 = \psi_0 \chi_\downarrow$. Here, we consider the excitation of an electron from either ϕ_1 or ϕ_2 to the orbital ϕ_ν .

Since, for this system, the exchange potential satisfies $v_x = -v_H/2 = -\langle \psi_0 | g | \psi_0 \rangle$, we obtain

$$\begin{aligned}\langle \phi_1 | v_x | \phi_1 \rangle &= \langle \phi_2 | v_x | \phi_2 \rangle \\ &= -\langle \psi_0 \psi_0 | g | \psi_0 \psi_0 \rangle = \langle \phi_1 | \hat{v}_x^{\text{HF}} | \phi_1 \rangle \\ &= \langle \phi_2 | \hat{v}_x^{\text{HF}} | \phi_2 \rangle,\end{aligned}$$

so that

$$\langle \phi_1 | \hat{v}_x^{\text{HF}} - v_x | \phi_1 \rangle = \langle \phi_2 | \hat{v}_x^{\text{HF}} - v_x | \phi_2 \rangle = 0,$$

and

$$\begin{aligned}\langle \phi_\nu | \hat{v}_x^{\text{HF}} - v_x | \phi_\nu \rangle &= -\langle \psi_\nu \psi_0 | g | \psi_0 \psi_\nu \rangle \\ &\quad + \langle \psi_\nu \psi_0 | g | \psi_\nu \psi_0 \rangle.\end{aligned}$$

Consequently, by combining the above equations and the formulae (Eqs. 10 and 11), we obtain a symmetrical splitting around the zeroth-order excitation energy:

$$\begin{aligned}\Delta E^{(1)}(T, 0 \rightarrow \nu) &= -\langle \psi_\nu \psi_0 | g | \psi_0 \psi_\nu \rangle, \\ \Delta E^{(1)}(S, 0 \rightarrow \nu) &= \langle \psi_\nu \psi_0 | g | \psi_0 \psi_\nu \rangle.\end{aligned}\tag{A4}$$

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