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Relationship of Kohn–Sham eigenvalues to excitation energies

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Abstract

In Kohn–Sham density functional theory, only the highest occupied eigenvalue has a rigorous physical meaning, viz., it is the negative of the lowest ionization energy. Here, we demonstrate that for finite systems, the unoccupied true Kohn–Sham eigenvalues (as opposed to the those obtained from the commonly used approximate density functionals) are also meaningful in that good approximations to excitation energies can be obtained from them. We argue that the explanation for this observed behavior is that, at large distances, the Kohn–Sham orbitals and the quasiparticle amplitudes satisfy the same equation to order $1/r^4$. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In the Kohn–Sham density functional method [1,2], the true interacting-electron system is replaced by a system of non-interacting electrons in an effective potential v_{eff}, defined by the requirement that the density of the non-interacting electrons equals the true density. The single particle orbitals and their eigenenergies were originally introduced as a mathematical artifact in order to achieve a good approximation to the kinetic energy, leaving only a relatively small term, the exchange-correlation energy E_{xc}, to be approximated in practical implementations of the theory. It was later shown [3–5] that the energy of the highest occupied orbital is in fact the negative of the ionization energy (provided the potential is defined such that it vanishes at infinity). However, most approximate functionals (such as the commonly used local density approximation [2]) yield poor approximations to it. The energies of the other occupied orbitals and of the unoccupied orbitals do not have a rigorous correspondence to excitation energies. Nevertheless, it is common practice to compare eigenvalue differences to optical spectra of molecules and solids. Since these comparisons are made using Kohn–Sham eigenvalues obtained from approximate exchange-correlation functionals, it is not clear how much of the discrepancy between theory and experiment would persist if the true Kohn–Sham eigenvalues were used. In this Letter we show that there is a surprising degree of agreement between the exact ground-state Kohn–Sham eigenvalue differences and excitation energies, for excitations from the highest occupied orbital to the unoccupied orbitals.

2. Method

The first step in the calculation is the evaluation of accurate densities. In the case of the 2-electron systems they were obtained [6] by numerically integrating wavefunctions (the wavefunction used [6] is a minor modification of that in Ref. [7]) which yield

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energies that are correct to 14 significant digits for He. In the case of Be, the density was obtained [8,9] by a combination of variational and diffusion Monte Carlo techniques, using a wavefunction that recovers 99.2% of the correlation energy in variational Monte Carlo and 99.9% of the correlation energy in diffusion Monte Carlo. Efficient implementations [10,11] of the variational and diffusion Monte Carlo methods are employed to rapidly sample the many-dimensional space of the wavefunctions.

The true Kohn–Sham potential is then obtained from the density. For the two-electron systems, it is obtained directly from the single-particle Kohn–Sham equation for the sole occupied orbital. For systems with more electrons, the potential is expanded in a set of functions and the expansion parameters varied such that the potential yields the true density [8,9,12]. All the Kohn–Sham eigenvalues can then be obtained by solving the Kohn–Sham equation.

3. Results

In Tables 1 and 2, we show the excitation energies of He and Be, respectively, obtained from differences of Kohn–Sham eigenvalues and compare them to the corresponding experimental energies. Note that a change of the Kohn–Sham potential by a constant will not affect the calculated excitation energies, as these are obtained as differences of eigenvalues. Of course, the single-electron Kohn–Sham energies do not distinguish between the energies within a multiplet. The energies obtained from the eigenvalue differences, lie between the experimental singlet and triplet excitation energies with the exception of only the (1s → 3d) 1D excitation for He (similar results have been obtained for Li$^+$. [13]). The calculated energies are for an infinite mass nucleus and do not include relativity, whereas the experimental numbers are, of course, for finite mass nuclei and are relativistic. In the case of the two-electron systems it is possible to calculate exceedingly accurate infinite nuclear mass non-relativistic total energies [14,15]. The excitation energies obtained from these calculations are also shown for He in Table 1. We observe that now even the (1s → 3d) 1D excitation energy of He obtained from the eigenvalue differences agrees with the true calculated excitation energy to the number of digits shown. To the best of our knowledge, this remarkable agreement between the Kohn–Sham eigenvalue differences and the excitation energies has not been noticed before, for any real system, though it has been noticed for a model semiconductor [16].

Table 1
Excitation energies of He in hartree atomic units

Transition	Final state	Experiment	Drake	$\Delta\epsilon_{KS}$
1s → 2s	$2\,^3\mathrm{S}$	0.72833	0.72850	0.7460
	$2\,^1\mathrm{S}$	0.75759	0.75775	
1s → 2p	$1\,^3\mathrm{P}$	0.77039	0.77056	0.7772
	$1\,^1\mathrm{P}$	0.77972	0.77988	
1s → 3s	$3\,^3\mathrm{S}$	0.83486	0.83504	0.8392
	$3\,^1\mathrm{S}$	0.84228	0.84245	
1s → 3p	$2\,^3\mathrm{P}$	0.84547	0.84564	0.8476
	$2\,^1\mathrm{P}$	0.84841	0.84858	
1s → 3d	$1\,^3\mathrm{D}$	0.84792	0.84809	0.8481
	$1\,^1\mathrm{D}$	0.84793	0.84809	
1s → 4s	$4\,^3\mathrm{S}$	0.86704	0.86721	0.8688
	$4\,^1\mathrm{S}$	0.86997	0.87014	

The theoretical energies of Drake and coworkers [14,15] and the eigenvalue differences are for infinite nuclear mass and neglect relativity. The experimental energies are from Ref. [17].

Table 2
Excitation energies of Be in hartree atomic units

Transition	Final state	Experiment	$\Delta\epsilon_{KS}$
2s → 2p	$1\,^3\mathrm{P}$	0.100153	0.1327
	$1\,^1\mathrm{P}$	0.193941	
2s → 3s	$2\,^3\mathrm{S}$	0.237304	0.2444
	$2\,^1\mathrm{S}$	0.249127	
2s → 3p	$2\,^3\mathrm{P}$	0.267877	0.2694
	$2\,^1\mathrm{P}$	0.274233	
2s → 3d	$1\,^3\mathrm{D}$	0.282744	0.2833
	$1\,^1\mathrm{D}$	0.293556	
2s → 4s	$3\,^3\mathrm{S}$	0.293921	0.2959
	$3\,^1\mathrm{S}$	0.297279	
2s → 4p	$3\,^3\mathrm{P}$	0.300487	0.3046
	$3\,^1\mathrm{P}$	0.306314	
2s → 4d	$2\,^3\mathrm{D}$	0.309577	0.3098
	$2\,^1\mathrm{D}$	0.313390	
2s → 5s	$4\,^3\mathrm{S}$	0.314429	0.3153
	$4\,^1\mathrm{S}$	0.315855	

The eigenvalue differences are for infinite nuclear mass and neglect relativity. The experimental energies are from Ref. [17].

It should be emphasised that the agreement exists only for accurate Kohn–Sham eigenvalues. Those obtained from popular approximate density functionals, such as the local density approximation (LDA) and various generalized gradient approximations (GGAs) are nowhere close to being sufficiently accurate. In fact, it is not even possible to make such a comparison with LDA or GGA orbitals because for neutral atoms the LDA or GGA potentials bind few, if any, unoccupied orbitals. This, of course, is due to the fact that the exchange-correlation potential of these approximate functionals decays considerably faster than $-1/r$.

4. Discussion

It should come as no surprise that the higher excitations are accurately given by the eigenvalue differences since that follows from the following two well-known facts. First, the highest occupied eigenvalue is exact, i.e. it is minus the ionization energy [3–5]. Second, the higher unoccupied eigenvalues approach a Rydberg series since the exchange-correlation potential approaches $-1/r$ at large distances. Hence, it is to be expected that the higher excitations will be progressively better approximated by the eigenvalue differences. However, this argument does not explain the agreement observed for the lower lying states. Second, the agreement for the higher lying states is better than can be explained by the above argument since the manner in which the eigenvalues approach the Rydberg limit is also in agreement with the excitation energies. The deviation of the eigenvalues from a Rydberg series is given by the quantum defect:

$$\delta_n = n - \sqrt{\frac{-1}{2\epsilon_n}}\ , \tag{1}$$

where ϵ_n is the n^{th} eigenvalue. Remarkably, it is found [18] that the quantum defects of Ne, calculated from the eigenvalues, agree rather well with the experimental quantum defects. Clearly some further explanation is needed.

We now argue that the explanation lies in the fact that the Kohn–Sham orbitals and quasiparticle amplitudes (defined below) satisfy the same equation, not only up to order $(1/r)$ but up to order $(1/r^4)$ inclusive. Of course the differences of the quasiparticle energies yield the true excitation energies. Consider an N-electron system in its i^{th} state Ψ_i^N, obtained by exciting an electron from the highest occupied level of the ground state Ψ_0^N. If we keep the 1st electron fixed, we have an $(N-1)$-electron function which we can expand in any complete basis set, with the expansion coefficients f being functions of the position of the 1st electron. Choosing the complete set to be the eigenstates of the $N-1$ electron system, we have

$$\Psi_i^N(r_1,r_2,\dots,r_N) = \sum_{j=0}^{\infty} f_{ij}(r_1)\,\Psi_j^{N-1} \times (r_2,\dots,r_N)\,. \tag{2}$$

The expression on the right hand side must be antisymmetric because the left hand side is. We will refer to the f_{ij} as quasiparticle amplitudes but we note that they are not the usual Dyson quasiparticle amplitudes.

At large distances, the quasiparticle amplitudes f_{i0} obey the equation

$$\left(-\frac{\nabla^2}{2} - \frac{(Z-N+1)}{r} + \frac{Q}{r^3} - \frac{\alpha}{2r^4} + \mathscr{O}\left(\frac{1}{r^5}\right)\right) f_{i0} = \left(E_i^N - E_0^{N-1}\right) f_{i0}\,, \tag{3}$$

where Q and α are the quadrupole moment and the dipole polarizability of the ground state Ψ_0^{N-1} of the $(N-1)$-electron system. Further it can be shown that

$$f_{ij} \sim f_{i0}/r^2 \quad \text{for} \quad j \neq 0\,. \tag{4}$$

Eqs. (3) and (4) are generalizations of equations obtained by Almbladh and von Barth [19] for the ground $(i=0)$ state of the N-electron system.

At large distances, the Kohn–Sham orbitals ϕ_i satisfy the equation

$$\left(-\frac{\nabla^2}{2} - \frac{(Z-N)}{r} + v_{\text{xc}}(r) + \mathscr{O}(\exp)\right)\phi_i = \epsilon_i \phi_i\,. \tag{5}$$

Now consider the densities resulting from the many-body quasiparticle equations and the Kohn–Sham equation:

$$\rho_i^{\text{MB}} = \sum_{j=0}^{\infty} f_{ij}^2 \to f_{i0}^2\left(1 + \mathscr{O}\left(\frac{1}{r^4}\right)\right) \quad \text{as} \quad r \to \infty, \tag{6}$$

$$\rho_0^{\text{KS}} = \sum_{j=1}^{N} \phi_j^2 \to \phi_N^2(1 + \mathscr{O}(\exp)) \quad \text{as} \quad r \to \infty. \tag{7}$$

Equating the ground state many-body and Kohn–Sham densities we obtain:

$$\rho_0^{\mathrm{KS}} = \rho_0^{\mathrm{MB}} \Rightarrow \begin{cases} \epsilon_N = \left(E_0^N - E_0^{N-1}\right) \\ \phi_N = f_{00}\left(1 + \mathcal{O}\left(\dfrac{1}{r^4}\right)\right) \\ v_{\mathrm{xc}} = -\dfrac{1}{r} + \dfrac{Q}{r^3} - \dfrac{\alpha}{2r^4} + \mathcal{O}\left(\dfrac{1}{r^5}\right). \end{cases} \tag{8}$$

The first of these follows from the fact that the exponential decay is governed only by the right hand side of Eqs. (3) and (5) and is the well-known result that the highest occupied KS eigenvalue yields the ionization energy [3–5]. The second of these follows from Eqs. (6) and (7). The third follows from relating the coefficients of a $1/r$ expansion of the density or equivalently the highest KS orbital to a $1/r$ expansion of v_{xc}. If the KS and the quasiparticle orbitals are equal to $\mathcal{O}(1/r^n)$, then it is easy to show that the potentials must be equal to $\mathcal{O}(1/r^{n+1})$

Of course all the KS orbitals satisfy the same equation, while the quasiparticle amplitudes all satisfy different equations, but the quasiparticle equations differ from each other and from the KS equation only at order $\mathcal{O}(1/r^5)$.

The question now arises: is the fact that the highest occupied eigenvalue is correct, plus the fact that the Kohn–Sham and the quasiparticle potentials agree to order $1/r^4$, sufficient to pin down the unoccupied eigenvalues with sufficient accuracy? We conjecture the answer is yes, at least for sufficiently smooth potentials. In order to provide evidence for our conjecture we constructed two model potentials both of which yield the true occupied Kohn–Sham eigenvalue for Helium. The first of these potentials agrees with the true Kohn–Sham potential to order $1/r$ while the second agrees up to order $1/r^4$. The procedure used to construct the model potentials has similarities to the standard procedure used to generate pseudopotentials but we do not impose the norm-conservation condition.

Table 3
Comparison of the Kohn–Sham eigenvalues for He with those with those of two model systems that have the same occupied eigenvalue and have potentials that agree with the He potential to order $1/r$ and $1/r^4$

Orbital	Model		Helium
	$\mathcal{O}(1/r)$	$\mathcal{O}(1/r^4)$	
1s	−0.9037	−0.9037	−0.9037
2s	−0.1748	−0.1588	−0.1577
2p	−0.1594	−0.1284	−0.1266
3s	−0.0696	−0.0648	−0.0645
3p	−0.0653	−0.0566	−0.0561
3d	−0.0621	−0.0557	−0.0556
4s	−0.0370	−0.0350	−0.0349

Motivated by the long-range asymptotic behavior of many-body wavefunctions [20,21], we construct these potentials by choosing the Kohn–Sham orbital to be

$$\psi \propto (r+1)^a \mathrm{e}^{-\zeta r}\left(1 + \sum_{i=1}^{3} \frac{q_i}{(r+1)^i}\right), \tag{9}$$

where $\zeta = \sqrt{2E_{\mathrm{ion}}}$, $a = Z_{\mathrm{eff}}/\zeta - 1$, $Z_{\mathrm{eff}} = Z - N + 1$, Z is the nuclear charge, N is the number of electrons and E_{ion} is the ionization energy. The Kohn–Sham potential that yields this orbital is obtained simply by solving the single-particle Shrödinger equation for the potential. The first potential, is obtained by setting $q_1 = q_2 = q_3 = 0$ and agrees with the true Kohn–Sham potential to order $1/r$. The second potential, has values of q_1, q_2, q_3 chosen to match the true Kohn–Sham potential to order $1/r^4$.

In Table 3, we compare the eigenvalues obtained from the two model potentials with the KS eigenvalues for He. It is apparent that the eigenvalues of the second model are closer, by a factor of 20 or more, to the eigenvalues of He than are the eigenvalues of the first model. The differences of the eigenvalues of the second model and those of He are of comparable magnitude to the differences of the true He Kohn-Sham eigenvalue differences from the excitation energies. Hence, it appears that our conjecture is correct. We have performed the same test for Li^+ and find similar results.

In conclusion we have discovered that excitations from the highest occupied orbital are in surprising agreement with differences of Kohn–Sham eigenvalues and we present a plausible explanation for this finding. The present results indicate that useful information about excited states could be obtained from ground-state single-particle energies provided that the approximate functional used, yields single-particle energies that are sufficiently close to the true Kohn–Sham values. Unfortunately the popular LDA and GGA functionals are nowhere near sufficiently accurate. The exact exchange-only potential, obtained from the optimized effective potential (OEP) method, does better [22] since it decays as $-1/r$ at large distances but it is much inferior to the true Kohn–Sham potential. Hence it is necessary to combine it with an accurate correlation potential but unfortunately all existing correlation functionals, which we have studied, yield potentials that bear little resemblance [8,9] to the true correlation potential. The Kohn–Sham eigenvalues are also the starting point for two more accurate methods for calculating excitation energies, namely time-dependent density functional theory [23–25] and density functional perturbation theory [22,26,27]. Again, the success of these methods (for all excitations except those within the same principal quantum number shell as the highest occupied level) relies on having functionals that yield good approximations to the true Kohn-Sham eigenvalues.

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