P H Y S I C A L   R E V I E W   L E T T E R S

Rydberg Transition Frequencies from the Local Density Approximation

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A method is given that extracts accurate Rydberg excitations from density functional calculations in the local density approximation, despite the short-ranged potential. For the case of He and Ne, the asymptotic quantum defects predicted by the calculations are in less than 5% error, yielding transition frequency errors of less than 0.1 eV.

The excitation energy spectrum of atoms, molecules, clusters, and solids can now be accurately calculated via time-dependent density functional theory (TDDFT) [1]. In Casida's matrix formulation [2], first the self-consistent solution of the ground-state Kohn-Sham (KS) equations is found [3], and the differences between occupied and unoccupied KS orbital energies may then be regarded as a first approximation to the true excitations of the system. In a second step, these KS frequencies are corrected to become the true transitions of the many-body system. The quality of the results depends crucially on the functional employed for the solution of the ground-state problem.

The local density approximation (LDA) is the simplest and historically most successful approximation in DFT [3]. Whereas new generations of functionals have achieved better accuracy than LDA for many properties, its ratio of reliability to simplicity has no paragon. But a well-known shortcoming of the ground-state LDA potential of an atom or molecule, already recognized by Tong and Sham in the early days of the LDA [4], is that it decays exponentially at large distances, rather than as $-1/r$ as the exact KS potential does. As a consequence, the LDA potential does not support a Rydberg series of bound states. Also, the magnitude of the highest occupied molecular orbital (HOMO) is typically too small by several eV in an LDA calculation, so HOMO $\rightarrow$ Rydberg transitions appear as HOMO $\rightarrow$ continuum excitations. Because of this limitation, several schemes have been devised to asymptotically correct the LDA potentials. Casida and Salahub (CS) [5] proposed a ''shift-and-splice'' approach consisting of shifting the LDA potential downwards in the bulk regions and joining it continuously with the van Leeuwen–Baerends potential [6] where they cross. Tozer and Handy (TH) proposed a very similar procedure [7] using a Fermi-Amaldi tail as suggested by Zhao, Morrison, and Parr [8], and a more sophisticated way to smoothen the transition from the inner to the outer potential. Wu, Ayers, and Yang (WAY) [9], noting that neither of these potentials yield an energy minimum, proposed a variational method for correcting the exchange-correlation (XC) potential. Their construction imposes the correct asymptotic behavior by using the Fermi-Amaldi form as

a fixed reference potential, and the coefficients of a linear combination of basis functions are determined through minimization of the energy for a given choice of energy functional. Their asymptotically corrected LDA potentials very closely resemble the pure LDA ones shifted downwards in energetically important regions. For any finite basis set, however, they are no longer functional derivatives of the LDA energy functional. Interestingly, the results obtained so far for excitation energies with the WAY method are not as good as those obtained with TH potentials that retain the pure LDA form in the core regions [10]. All of these methods have improved upon LDA on the prediction of Rydberg excitation frequencies, leading to the conclusion that the correct long-range behavior of the potentials is indispensable to describe such excitations. But we show here that in fact *it is not*.

The purpose of the present Letter is to show how the Rydberg excitation energies are encoded in the short-ranged LDA potentials. Imposing the correct asymptotic behavior is one way to decode them, but not the best one, since different tails lead to different answers (e.g., van Leeuwen–Baerends vs Fermi-Amaldi), obscuring the information provided by a *pure* LDA calculation.

It was recently shown [11] that in spite of incorrectly describing photoabsorption as if it were photoionization, the oscillator strengths of Rydberg excitations show up in the LDA spectrum as continuum contributions with excellent optical intensity. The dipole matrix elements for HOMO $\rightarrow$ Rydberg transitions are accurate in LDA because (1) the shape of the LDA HOMO is very close to that of the exact KS HOMO, even if its energy is not, and (2) LDA continuum orbitals at frequencies corresponding to HOMO $\rightarrow$ Rydberg transitions, are also very close to the exact KS Rydberg orbitals in the crucial region for optical absorption, i.e., where the HOMO has high amplitude. The underlying physical reason for this is simple [11]: the LDA XC potential is very close to the exact XC potential near the nuclei, and runs almost parallel to it in the valence regions [12].

An obvious objection to this claim of success of the LDA is that it cannot predict the *positions* of the Rydberg excitations, even if it produces an ionization envelope that

approximates well the discrete photoabsorption spectrum. We now show that, in fact, LDA *does* predict the position of high-n Rydberg excitations very accurately. We use concepts of quantum defect theory, developed before the advent of DFT by Ham [13] and Seaton [14]. The quantum defect μ_{nl} parametrizes the energy E_{nl} of a Rydberg state as

$$E_{nl} = -\frac{1}{2(n - \mu_{nl})^2}. \tag{1}$$

For an electron orbiting in a Coulomb field outside an ionic core, as in a high-n Rydberg state, μ_{nl} represents the effect of the field that prevails *within* the core. Although the Coulomb field outside the core is invoked for its definition in Eq. (1), the actual number μ_{nl} is determined only by the forces within [15]. It is typically a very smooth function of n, and approaches rapidly the asymptotic quantum defect, $\mu_{\infty l}$, as $n \to \infty$.

We will focus on the KS asymptotic quantum defect of the ($l = 0$) Rydberg series that converges to the first ionization threshold of an atom (the $l = 0$ subscript will be dropped from now on). We first propose a method to extract μ_n from a given orbital, and illustrate it with a simple example. This method was inspired by Fano's original discussion in Ref. [15]. We then apply it to the cases of He and Ne, where the exact KS quantum defects are known, and show that the LDA produces μ_∞'s which are in less than 5% error.

Quantum defect from an orbital.—Consider a long-range potential that equals $-1/r$ for $r \geq r_0$. The solution of the radial Schrödinger equation is well known for $r \geq r_0$. For negative energies $E < 0$, the physically acceptable solutions are Whittaker functions (we will restrict the analysis to s states):

$$\phi_{>r_0}(r) = A W_{1/k,1/2}(2kr), \tag{2}$$

where A is a constant and $k = \sqrt{2|E|}$. The logarithmic derivative of $\phi_{>r_0}$ is given by

$$\frac{d \ln \phi_{>r_0}}{dr} = \frac{1}{n^*} - \frac{n^*}{r} - \frac{1}{r}\frac{U(-n^*; 2; 2r/n^*)}{U(1 - n^*; 2; 2r/n^*)}. \tag{3}$$

Here k was written as $k = (n^*)^{-1}$, with $n^* = (n - \mu_n)$, where n numbers the bound state, and μ_n is the quantum defect; U is the confluent hypergeometric function [16].

Regardless of the shape of the potential for $r < r_0$, the logarithmic derivative of $\phi_{<r_0}$ must equal that of $\phi_{>r_0}$ at r_0. Now suppose that an orbital is given to us, with the information that it is the $n = 8$ state of a potential that possesses a Coulomb tail. We can immediately obtain μ from this orbital by solving Eq. (3) numerically, using $n = 8$ and some large value of r. If we observe that $\mu(r)$ changes as r is increased, we can conclude that Eq. (3) is being used in the region where $r < r_0$, and its solution cannot be interpreted as the quantum defect.

For example, consider a potential which is equal to a constant C for $r < r_0$ and to $-1/r$ for $r \geq r_0$. For $r_0 = 1$ the matching condition is

$$\tilde{k} \coth \tilde{k} = \frac{1}{n^*} - n^* - \frac{U(-n^*; 2; 2/n^*)}{U(1 - n^*; 2; 2/n^*)}, \tag{4}$$

where $\tilde{k} = \sqrt{2|E - C|}$. Equation (4) was solved for the first 20 bound states. For $C = r_0 = 1$ the asymptotic quantum defect is $\mu_\infty = -0.441$, see Fig. 1. Figure 2 shows $\mu(r)$, the solution of Eq. (3) as a function of r, for the $n = 20$ orbital. Clearly, the quantum defect for a given state can be obtained by looking at the respective orbital anywhere in the region $r > r_0$. In particular, it can be obtained *at* r_0. It represents the accumulation of phase due to the non-Coulombic potential in the region of $r < r_0$ up to $r = r_0$.

Imagine now that the potential is altered by truncating the Coulomb tail far away, at $r_1 \gg r_0$, and making the potential equal to the constant $-1/r_1$ for all $r > r_1$. This modified potential has an orbital which—up to a constant—is almost identical to the original $n = 20$ Rydberg orbital in the region $r < r_0$, but it may now be a *scattering* orbital, behaving very differently in the region $r > r_1$. We can *still* solve Eq. (3) on this scattering orbital, with $n = 20$ on the right-hand side, and find $\mu \simeq -0.441$ at r_0. The altered potential does not have a Rydberg series, yet the solution of Eq. (3) at r_0 can still be interpreted as the asymptotic quantum defect of the Rydberg series that was lost as a consequence of the alteration.

The Coulomb tail has nothing to do with the *value* of μ. It only has to do with its definition.

One technical point deserves comment: rather than giving $\mu(r)$ directly, Eq. (3) yields $n^*(r)$, and it would seem that it needs to be solved with ever increasing accuracy as $n \to \infty$, since orbitals of different n become essentially identical at large n in the $[0, r_0]$ region. Only the fractional part of the solution of Eq. (3) is to be trusted, yielding the fractional part of n^*, which is also equal to the fractional part of the asymptotic quantum defect, denoted $\{\mu_\infty\}$. The integer part of μ_∞ can be determined by a simple node counting as $[\mu_\infty] = N - N_C$, where N is the number of
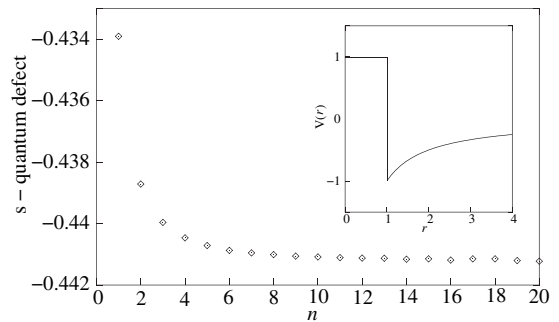

FIG. 1. s-quantum defect as a function of n for the potential shown in the inset. The quantum defect is a smooth function of n and converges rapidly to its asymptotic value, $\mu_\infty = -0.441$.
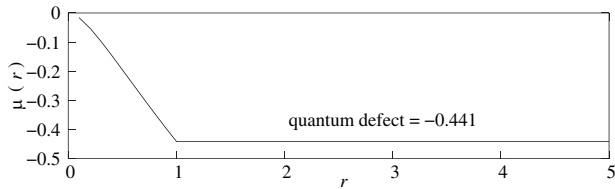
FIG. 2.   Solution of Eq. (3) for μ as a function of r, for the potential of Fig. 1; the logarithmic derivative of the $n = 20$ orbital was found numerically as a function of r, and at each location r, it was inserted into Eq. (3) to get $\mu(r)$.

nodes of the given orbital in the $[0, r_0]$ interval and N_C that of the corresponding pure Coulomb orbital. The asymptotic quantum defect $\mu_\infty = [\mu_\infty] + \{\mu_\infty\}$ is thus fully determined this way.

Results for helium and neon.—Consider the first s-Rydberg series of the He atom. Figure 3 shows the s-quantum defect as a function of n from the *exact* KS potential obtained by Umrigar and Gonze [17]. The asymptotic quantum defect $\mu_\infty = 0.213$ can be extracted through Eq. (3) from, e.g., the $n = 20$ orbital, just as it was done in the previous example. It is clear from the solid line of Fig. 4 that at $r_0 \sim 1$, Eq. (3) is already giving an accurate value of μ, which is quite remarkable considering that the KS potential at $r \sim 1$ is still not equal to $-1/r$ (see Fig. 5). Most of the quantum defect is built up close to the nucleus (steep rise for $0 < r < 1$ in Fig. 4), and its final value has been reached before the potential becomes purely Coulombic.

The LDA potential runs almost parallel to the exact one in the region $1 < r < 2$ (where μ_∞ can already be extracted accurately), and orbitals corresponding to the same *frequency* (exact and LDA) are therefore very close in that region, see Fig. 6. In the spirit of Ref. [11], we compare the exact energy-normalized $20s$ orbital (which is essentially identical to the zero-energy state in the region $0 < r < 6$) and the LDA orbital of energy $I + \epsilon_{1s}^{\mathrm{LDA}} = 0.904 - 0.571 = 0.333$. Notice how good the LDA orbital is in the region $1 < r < 2$. We show in Fig. 4 the solution of Eq. (3) when this scattering LDA orbital is employed. Clearly, the plateau of the LDA curve in the $1 < r < 2$ region is an accurate estimate of the quantum defect. The value of μ on this plateau is 0.205, an underestimation of less than 4% with respect to the exact value.
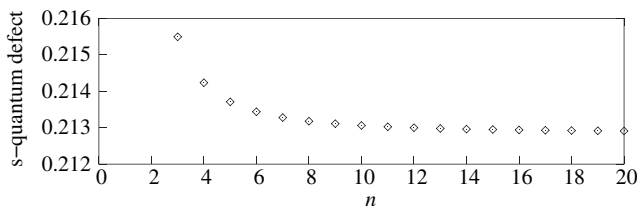

FIG. 3. s-quantum defect as a function of n for the exact KS potential [17] of the He atom. The quantum defect converges rapidly to its asymptotic value, $\mu_\infty = 0.213$.
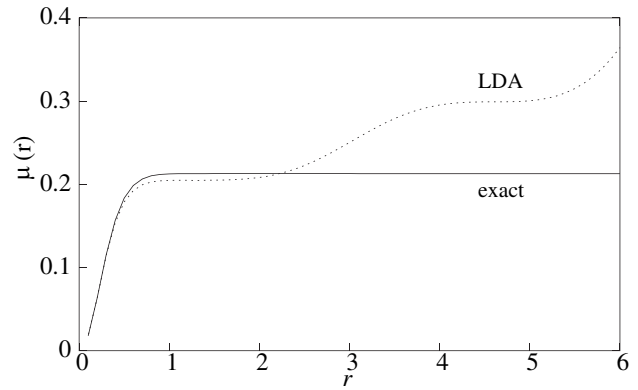

FIG. 4.   He atom: solution of Eq. (3) for μ as a function of r; The $n = 20$ orbital was used for the exact case, and the scattering orbital of energy $E = I + \epsilon_{1s}^{\mathrm{LDA}}$ was used for the LDA.

Thus, given the ionization potential of the system, LDA gives a very accurate prediction of the asymptotic quantum defect. The ionization potential is needed to choose the appropriate LDA scattering orbital, but the results are not terribly sensitive to it. We repeated the same procedure with the LDA ionization potential [defined as $E_{\mathrm{LDA}}(\mathrm{He}) - E_{\mathrm{LDA}}(\mathrm{He}^+) = 0.974$] instead of the exact one, and found $\mu_\infty^{\mathrm{LDA}} = 0.216$, overestimating the exact μ_∞ by just 1%.

Our analysis provides a natural way to asymptotically correct the LDA potential: simply force the LDA plateau of Fig. 4 to stay constant for all r. The resulting function $\mu(r)$ determines a zero-energy orbital which in turn uniquely determines a potential through inversion of the Kohn-Sham equations at zero energy. We emphasize, however, that such potential is not needed to obtain μ_∞, but the question of what long-range potential gives rise to the same μ_∞ is certainly worth addressing. The TH [7] or CS [5] methods for asymptotically correcting the LDA potentials require choosing a radius r_0 where the proper tail is to be pasted.
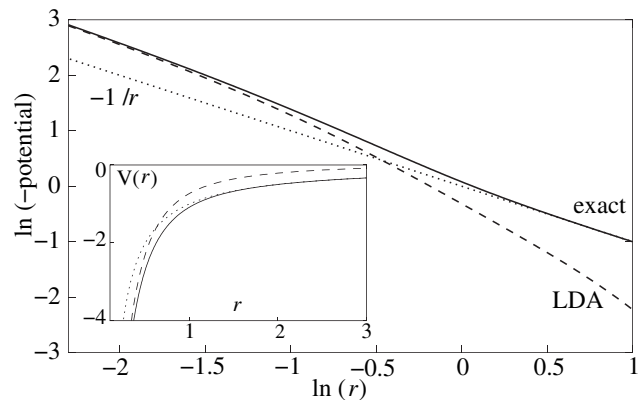

FIG. 5.   Comparison of the exact KS potential of the He atom [17] (solid line), and the LDA potential (dashed line). The Coulomb potential is also shown (dotted line). At $r \sim 1$ the exact potential is almost Coulombic. The inset shows the potentials themselves.
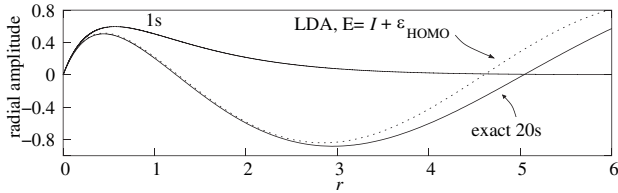
FIG. 6. Radial orbitals of He: LDA orbital of energy $E = 0.333$ and exact 20 s orbital; the HOMO is also shown. The LDA scattering orbital and the exact KS Rydberg orbital are very close in the region $1 < r < 2$, where the quantum defect can be extracted (see text, and Fig. 4). The fact that the LDA orbital has an incorrect asymptotic behavior at large r is irrelevant for the value of μ, as well as for optical absorption [11].

Our analysis also provides a way to rigorously justify such choice, since r_0 should clearly be on the LDA plateau of $\mu(r)$. Minimizing $d\mu(r)/dr|_{r_0}$ determines its precise value of $r_0 \sim 1.3$. To test this, we performed a simple Latter-type asymptotic correction [18] by pasting a $-1/r$ tail to the LDA potential shifted downwards by $v_{\text{LDA}}(r_0) - r_0^{-1}$, and scanning through r_0. The errors in both μ_∞ and ϵ_{1s} were minimized at $r_0 \sim 1.5$.

Repeating the same procedure for the Ne atom we found again a distinctive plateau in the LDA curve of $\mu_\infty(r)$ at $\mu_\infty^{\text{LDA}} = 1.366$, an overestimation of 4% with respect to the exact value ($\mu_\infty^{\text{exact}} = 1.313$).

It has been shown [19] for the case of Ne that 3 numbers are enough to fit very accurately the entire curve of Kohn-Sham quantum defects of a given l. Although we have only determined one such number here (μ_∞), we use it nonetheless to approximate all the $l = 0$ KS orbital energies as $\epsilon_{\text{LDA}}^{\text{approx}} = -[2(n - \mu_\infty)]^{-1}$. The results are presented in Table I. The errors are smaller than typical TDDFT errors [1].

Finally, our results suggest that the LDA can also be employed to calculate accurate low-energy electron-ion scattering phase shifts. In fact, the LDA asymptotic quantum defect found in this work, $\mu_\infty^{\text{LDA}} = 0.205$, immediately

yields, through Seaton's theorem [14], a prediction for the zero-energy s-phase shift for electron-He$^+$ scattering: $\delta(E = 0)_{\text{LDA}} = \pi\mu_\infty^{\text{LDA}} = 0.644$. The *exact* KS phase shift is $\delta(E = 0)_{\text{exact}} = 0.669$. This value is also remarkably close to the average of the experimental singlet/triplet zero-energy phase shifts [20].

In conclusion, we have shown that rather than modifying the shape of the LDA potentials one can modify the interpretation of the results of a *pure* DFT-LDA calculation. The results are excellent for the excitation to high-lying s-Rydberg states in He and Ne, and we are working to extend these ideas to Rydberg excitations in molecules.

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TABLE I. Transition frequencies (in eV) for the first six discrete $2p \rightarrow ns$ transitions in Ne, from the exact and LDA KS potentials.

Transition	Transition Frequency	
	LDA	Exact
$2p \rightarrow 3s$	16.468	16.604
$2p \rightarrow 4s$	19.603	19.666
$2p \rightarrow 5s$	20.534	20.561
$2p \rightarrow 6s$	20.931	20.945
$2p \rightarrow 7s$	21.135	21.143
$2p \rightarrow 8s$	21.255	21.260