Rydberg transition frequencies from the Local Density Approximation

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

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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 [4]. Whereas new generations of functionals have achieved better accuracy than LDA for many properties, its ratio of reliability to simplicity has no paragon. But we show here 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 work 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 $\text{HOMO} \rightarrow \text{Rydberg}$ 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 $\text{HOMO} \rightarrow \text{Rydberg}$ 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\cite{13} and Seaton\cite{20}. The quantum defect $\mu_{nl}$ parametrizes the energy $E_{nl}$ of a Rydberg state as:

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

For an electron orbiting in a Coulomb field outside an ionic core, as in a high-$n$ Rydberg state, $\mu_{nl}$ 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.\ref{1}, the actual number $\mu_{nl}$ is determined only by the forces within\cite{15}. It is typically a very smooth function of $n$, and approaches rapidly the asymptotic quantum defect, $\mu_{\infty}$, 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 $\mu_{\infty}$ from a given orbital, and illustrate it with a simple example. This method was inspired by Fano’s original discussion in Ref.\cite{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 $\mu_{\infty}$’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): 

$$\phi_{>r_0}(r) = AW_{1/k,1/2}(2kr),$$ \hfill (2)

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

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

Here $k$ was written as $k = (n^*)^{-1}$, with $n^* = (n - \mu_n)$, where $n$ numbers the bound state, and $\mu_n$ is the quantum defect; $U$ is the confluent hypergeometric function\cite{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 $\mu$ from this orbital by solving Eq.\ref{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.\ref{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:

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

where $\tilde{k} = \sqrt{2(|E| - C)}$. Eq.\ref{3} was solved for the first 20 bound states. For $C = r_0 = 1$ the asymptotic quantum defect is $\mu_{\infty} = -0.441$, see Fig\ref{1}. Figure\ref{2} shows $\mu(r)$, the solution of Eq.\ref{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 $r_1 >> r_0$, 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.\ref{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.\ref{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.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{s-quantum_defect.png}
\caption{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, $\mu_{\infty} = -0.441$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{solution.png}
\caption{Solution of Eq.\ref{3} for $\mu$ as a function of $r$, for the potential of Fig\ref{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.\ref{3} to get $\mu(r)$.}
\end{figure}
The Coulomb tail has nothing to do with the value of $\mu$. It only has to do with its definition.

One technical point deserves comment: rather than giving $\mu(r)$ directly, Eq. (3) yields $n^\ast(r)$, 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 $n^\ast$, which is also equal to the fractional part of the asymptotic quantum defect, denoted $\{\mu_\infty\}$. The integer part of $\mu_\infty$ can be determined by a simple node counting as $[\mu_\infty] = N - N_C$, where $N$ is the number of 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 $n$ for the exact KS potential obtained by Umrigar and Gonze. 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 $\mu$, which is quite remarkable considering that the KS potential at $r \sim 1$ is still not equal to $-1/r$ (see Fig. 4). 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 $\mu_\infty$ can already be extracted accurately), and orbitals corresponding to the same frequency (exact and LDA) are therefore very close in that region, see Fig. 4. 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 $E + \epsilon_{20s}^{\mu_\infty} = 0.904 - 0.571 = 0.333$. 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 $\mu$ on this plateau is 0.205, an underestimation of less than 4% with respect to the exact value.

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 $E_{\text{LDA}}(\text{He}) - E_{\text{LDA}}(\text{He}^+) = 0.974$) instead of the exact one, and found $\mu_\infty^{\mu_{\text{LDA}}} = 0.216$, overestimating the exact $\mu_\infty$ 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 $\mu_\infty$. 

FIG. 3: s-quantum defect as a function of $n$ for the exact KS potential [15] 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 $\mu$ as a function of $r$; The $n = 20$ orbital was used for the exact case, and the scattering orbital or energy $E = I + \epsilon_1^{\text{LDA}}$ was used for the LDA.

FIG. 5: Comparison of the exact KS potential of the He atom [12] (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.
TABLE I: Transition frequencies (in eV) for the first six discrete $2p \rightarrow ns$ transitions in Ne, from the exact and LDA KS potentials.

| trans. | 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 |

but the question of what long-range potential gives rise to the same $\mu_\infty$ is certainly worth addressing. The TH [7] or CS [8] methods for asymptotically correcting the LDA potentials require choosing a radius $r_0$ where the proper tail is to be pasted. 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 [15] by pasting a $-1/r$ tail to the LDA potential shifted downwards by $\nu LDA (r_0) - r_0^{-1}$, and scanning through $r_0$. The errors in both $\mu_\infty$ and $\varepsilon_{1s}$ 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 $\mu_\infty^{LDA} = 1.366$, an overestimation of 4% with respect to the exact value ($\mu_\infty^{exact} = 1.313$). It has been shown [10] 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 ($\mu_\infty$), we use it nonetheless to approximate all the $l = 0$ KS orbital energies as $\varepsilon_{l, LDA}^{approx} = -[2(n - \mu_\infty)]^{-1}$. The results are presented in Table II. The errors are smaller than typical TDDFT errors [10].

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, $\mu_\infty^{LDA} = 0.205$, immediately yields, through Seaton’s theorem [20], a prediction for the zero-energy $s$-phase-shift for electron-He$^+$ scattering: $\delta(E = 0)_{LDA} = \pi \mu_\infty^{LDA} = 0.644$. The exact KS phase shift is $\delta(E = 0)_{exact} = 0.669$. This value is also remarkably close to the average of the experimental singlet/triplet zero-energy phase shifts [21].

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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[1] E. Runge and E.K.U. Gross, Phys. Rev. Lett. 52, 997 (1984); M. Petersilka, U.J. Gossmann, and E.K.U. Gross, Phys. Rev. Lett. 76, 1212 (1996); J. Werschnik, E.K.U. Gross, and K. Burke, to appear in J. Chem. Phys. (2005).
[2] M.E. Casida, in Recent developments and applications in density functional theory, ed. J.M. Seminario (Elsevier, Amsterdam, 1996).
[3] W. Kohn and L.J. Sham, Phys. Rev. 140, A 1133 (1965).
[4] B.Y. Tong and L.J. Sham, Phys. Rev. 144, 1 (1966).
[5] M.E. Casida, D.R. Salahub, J. Chem. Phys. 113, 8918 (2000).
[6] R. van Leeuwen and E.J. Baerends, Phys. Rev. A. 49, 2421 (1994).
[7] D.J. Tozer and N.C. Handy, J. Chem. Phys. 109, 10180 (1998).
[8] Q. Zhao, R.C. Morrison, and R.G. Parr, Phys. Rev. A 50, 2138 (1994).
[9] Q. Wu, P.W. Ayers, and W. Yang, J. Chem. Phys. 119, 2978 (2003).
[10] Q. Wu, A.J. Cohen, and W. Yang, Molec. Phys. 103, 711 (2005).
[11] A. Wasserman, N.T. Maitra, and K. Burke, Phys. Rev. Lett. 91, 263001 (2003).
[12] J.P. Perdew, in Density Functional Methods in Physics, edited by R.M. Dreizler and J. da Providencia (Plenum, New York, 1995), p.265.
[13] F. Ham, Solid State Phys. 1, 127 (1955).
[14] M.J. Seaton, Mon. Not. R. Astron. Soc. 118, 504 (1958).
[15] U. Fano, Comments Atom. Mol. Phys. 10, 223 (1981).
[16] L.J. Slater, in Handbook of Mathematical Functions, ed. M. Abramowitz and I.A. Stegun, Dover, New York (1970), p.505.
[17] C. J. Umrigar and X. Gonze, Phys. Rev. A 50, 3827 (1994).
[18] R. Latter, Phys. Rev. 99, 510 (1955).
[19] A. I. Al-Sharif, R. Resta, C.J. Umrigar, Phys. Rev. A 57, 2466 (1998).
[20] M.J. Seaton, Mon. Not. R. Astron. Soc. 118, 504 (1958).
[21] A. Wasserman, N.T. Maitra, and K. Burke, J. Chem. Phys. 122, 133103 (2005).