HTML ABSTRACT + LINKS

Continuum states from time-dependent density functional theory

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Linear response time-dependent density functional theory is used to study low-lying electronic continuum states of targets that can bind an extra electron. Exact formulas to extract scattering amplitudes from the susceptibility are derived in one dimension. A single-pole approximation for scattering phase shifts in three dimensions is shown to be more accurate than static exchange for singlet electron-He^+ scattering. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1877052]

I. INTRODUCTION

Ground-state density functional theory (DFT) (Refs. 1 and 2) has become a popular electronic structure method in both quantum chemistry and solid-state physics, because modern approximations produce useful accuracy at moderate computational cost.[3,4] Now, electronic excitation energies of atoms and molecules are being calculated using linear response time-dependent density functional theory (TDDFT).[5,6] In this scheme, bound→bound transition energies are first approximated by the poles of the frequency-dependent Kohn–Sham (KS) density response function,[6–8] and then corrected to the poles of the true response function, i.e., the true excitations. Bound→continuum transitions, however, have not been treated in the same way because branch cuts of the KS and interacting response functions overlap, and because it is the phase shifts, rather than the energies, that are of interest in the scattering regime.

Even though photoresponse was addressed in the early days of TDDFT,[9] and there has been a long interest of using density functional methods for the scattering problem (e.g., Ref. 10), there is no formal theory based on TDDFT to study electron scattering. Such a theory might be particularly useful in the emergent field of electron-impact chemistry,[11] in which large targets are struck by low energy electrons, so that bound-free correlations are significant.[12]

Several results relevant to this goal are presented here. First, we provide a proof of principle: the time-dependent response of an N-electron ground state contains the scattering information for an electron scattering from the $(N-1)$-electron target, and this is accessible via TDDFT. Second, we show how this leads to practical ways of calculating scattering phase shifts or, in one dimension, transmission amplitudes. Finally, in the simplest case, singlet scattering from He^+, we find that TDDFT yields better results than static exchange, demonstrating its higher accuracy at low computational cost.

Although we are not presenting a *complete* theory of electron scattering within TDDFT, such a theory can be built upon the rigorous results presented here, and become a competitive alternative to existing techniques for calculating electron-molecule scattering cross sections (e.g., Ref. 13). Since continuum states are the current-carrying states in molecular electronic devices, we also anticipate applications of our one-dimensional (1D) results in the field of electronic transport through molecular wires.[14]

II. EXTRACTING SCATTERING INFORMATION FROM THE SUSCEPTIBILITY

A. Theory

Our starting point is the Dyson-like response equation that relates the susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ of a system of N interacting electrons with that of its ground-state KS analog, $\chi_s(\mathbf{r},\mathbf{r}';\omega)$.[6] In operator form ($*$ indicates spatial and spin convolution):

$$\chi = \chi_s + \chi_s * f_{\mathrm{HXC}} * \chi, \tag{1}$$

where f_{HXC} is the Hartree-exchange-correlation kernel (we use atomic units throughout):

$$f_{\mathrm{HXC}}[\rho](\mathbf{r},\mathbf{r}';t-t') \equiv \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} + \left.\frac{\delta v_{\mathrm{XC}}(\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\right|_{\rho}, \tag{2}$$

a functional of the N-electron ground-state density $\rho(\mathbf{r})$. In Eq. (2), $v_{\mathrm{xc}}(\mathbf{r},t)$ is the time-dependent exchange-correlation potential induced when a time-dependent perturbation is applied to the N-electron ground state. We write the spin-decomposed susceptibility in the Lehman representation:

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$$\chi_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) = \left[\sum_n \frac{F_{n\sigma}(\mathbf{r})F^*_{n\sigma'}(\mathbf{r}')}{\omega - \Omega_n + i0^+} + cc(\omega \to -\omega) \right], \tag{3}$$

with

$$F_{n\sigma}(\mathbf{r}) = \langle \Psi_0 | \hat{\rho}_\sigma(\mathbf{r}) | \Psi_n \rangle, \quad \hat{\rho}_\sigma(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{r}}_i)\delta_{\sigma\hat{\sigma}_i}, \tag{4}$$

where Ψ_0 is the ground state of the N-electron system, Ψ_n its nth excited state, and $\hat{\rho}_\sigma(\mathbf{r})$ is the σ-spin density operator. In Eq. (3), Ω_n is the $\Psi_0 \to \Psi_n$ transition frequency.

For the remainder of this section, we restrict the analysis to one dimension. Consider large distances, where the N-electron ground-state density is dominated by the decay of the highest occupied KS orbital;[15] the ground-state wave function behaves as[16]

$$\Psi_0 \underset{x\to\infty}{\to} \psi_0^{N-1}(x_2, \ldots, x_N) \sqrt{\frac{\rho(x)}{N}} S_0(\sigma, \sigma_2, \ldots, \sigma_N), \tag{5}$$

where ψ_0^{N-1} is the ground-state wave function of the $(N-1)$-electron system (the *target*), S_0 the spin function of the ground state, and $\rho(x)$ the N-electron ground-state density. Similarly,

$$\Psi_n \underset{x\to\infty}{\to} \psi_{n_t}^{N-1}(x_2, \ldots, x_N) \frac{\phi_{k_n}(x)}{\sqrt{N}} S_n(\sigma, \sigma_2, \ldots, \sigma_N), \tag{6}$$

where $\psi_{n_t}^{N-1}$ is an eigenstate of the target (labeled by n_t), S_n is the spin function of the nth excited state, and $\phi_{k_n}(x)$ a one-electron orbital.

We focus on elastic scattering, so the contribution to $F_{n\sigma}(x)$ from channels where the target is excited vanishes as $x \to \infty$ due to orthogonality. Inserting Eqs. (5) and (6) into the 1D version of Eq. (4), and taking into account the antisymmetry of both Ψ_0 and Ψ_n,

$$F_{n\sigma}(x) \underset{x\to\infty}{\to} \sqrt{\rho(x)}\phi_{k_n}(x)\delta_{0,n_t} \times \sum_{\sigma_2 \cdots \sigma_N} S_0^*(\sigma \cdots \sigma_N) S_n(\sigma \cdots \sigma_N). \tag{7}$$

The susceptibility at large distances is then obtained by inserting Eq. (7) into Eq. (3):

$$\begin{aligned} \chi(x,x';\omega) &= \sum_{\sigma\sigma'} \chi_{\sigma\sigma'}(x,x';\omega) \\ &\underset{x,x'\to\pm\infty}{\to} \sqrt{\rho(x)\rho(x')} \\ &\times \sum_n \frac{\phi_{k_n}(x)\phi^*_{k_n}(x')}{\omega - \Omega_n + i\eta} \delta_{0,n_t}\delta_{S_0,S_n} \\ &+ cc(\omega \to -\omega). \end{aligned} \tag{8}$$

Since only scattering states of the N-electron optical potential contribute to the sum in Eq. (8) at large distances, it becomes an integral over wave numbers $k = \sqrt{2\varepsilon}$, where ε is the energy of the projectile electron:

$$\sum_n \frac{\phi_{k_n}(x)\phi^*_{k_n}(x')}{\omega - \Omega_n + i\eta} \underset{x,x'\to\pm\infty}{\to} \frac{1}{2\pi} \int_{0[R],[L]}^{\infty} \frac{\phi_k(x)\phi^*_k(x')}{\omega - \Omega_k + i\eta} dk. \tag{9}$$

In this notation, the functions ϕ_{k_n} are box normalized and $\phi_{k_n}(x) = \phi_k(x)/\sqrt{L}$, where $L \to \infty$ is the length of the box. The transition frequency $\Omega_n = E_n^N - E_0^N$ is now simply $\Omega_k = E_0^{N-1} + k^2/2 - E_0^N = k^2/2 + I$, where I is the first ionization potential of the N-electron system, and E_0^M and E_n^M are the ground and nth excited state energies of the M-electron system. The subscript "[R], [L]" implies that the integral is over both orbitals satisfying *right* and *left* boundary conditions:

$$\phi_k^{[R]}(x) \to \begin{cases} e^{\pm ikx} + r_k e^{\mp ikx}, & x \to \mp\infty \\ t_k e^{\pm ikx}, & x \to \pm\infty. \end{cases} \tag{10}$$

When $x \to -\infty$ and $x' = -x$ the integral of Eq. (9) is dominated by a term that oscillates in space with wave number $2\sqrt{2(\varepsilon - I)}$ and amplitude given by the transmission amplitude for spin-conserving collisions t_k at that wave number. Denoting this by χ^{osc}, we obtain

$$t(\varepsilon) = \lim_{x\to-\infty} \left[\frac{i\sqrt{2\varepsilon}}{\sqrt{\rho(x)\rho(-x)}} \chi^{\text{osc}}(x, -x; \varepsilon + I) \right]. \tag{11}$$

While this formula also applies to the KS system, its transmission $t_s(\varepsilon)$ can be easily obtained by solving a *potential scattering* problem (i.e., scattering off the N-electron ground-state KS potential). The exact amplitudes $t(\varepsilon)$ of the many-body problem are formally related to the $t_s(\varepsilon)$ through Eqs. (11) and (1). This is the main result of this work: the time-dependent response of the N-electron ground state contains the scattering information, and is accessible via TDDFT. A potential scattering problem is solved first for the N-electron ground-state KS potential, and the scattering amplitudes thus obtained are further corrected by f_{HXC} to account for, e.g., polarization effects.

While Eq. (11) seems impractical as a basis for computations, it leads to practical approximations. For example, if Eq. (1) is iterated once, we find through Eq. (11) the following useful distorted-wave-Born-type approximation for the transmission amplitude:

$$t(\varepsilon) = t_s(\varepsilon) + \frac{1}{i\sqrt{2\varepsilon}} \langle\langle \text{HOMO}, \varepsilon | \hat{f}_{\text{HXC}}(\varepsilon + I) | \text{HOMO}, \varepsilon \rangle\rangle, \tag{12}$$

where $|\text{HOMO}, \varepsilon\rangle\rangle$ is the product of the highest occupied KS orbital and the continuum KS orbital of energy ε.

B. Example

We illustrate on a simple 1D model of an electron scattering from a one-electron atom of nuclear charge Z (Ref. 17) in the weak interaction limit:

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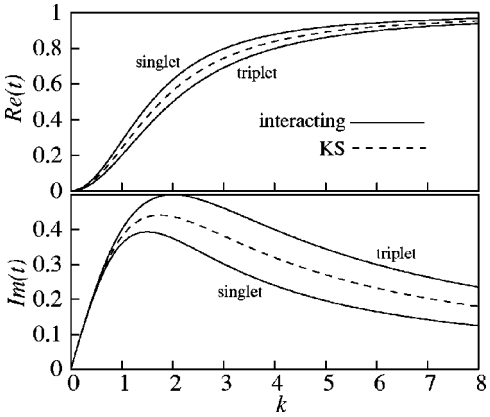

FIG. 1. Real and imaginary parts of the KS transmission amplitude t_s, and of the interacting singlet and triplet amplitudes (to first order in λ), for the model system of Eq. (13). $Z=2$ and $\lambda=0.5$ in this plot.

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{1}{2}\frac{d^2}{dx_2^2} - Z\delta(x_1) - Z\delta(x_2) + \lambda\delta(x_1 - x_2). \tag{13}$$

Electrons interact via a δ-function repulsion, scaled by λ. With $\lambda=0$ the ground state density is a simple exponential, analogous to hydrogenic atoms in 3D.

Exact solution in the weak interaction limit. First, we solve for the exact transmission amplitudes to first order in λ using the static exchange method.[18] The results for triplet t_{trip} and singlet t_{sing} scattering are

$$t_{trip} = t_0, \quad t_0 = \frac{ik}{Z + ik},$$
$$t_{sing} = t_0 + 2\lambda t_1, \quad t_1 = \frac{-ik^2}{(k - iZ)^2(k + iZ)}. \tag{14}$$

Our TDDFT solution. The ground-state of the N-electron system ($N=2$) is given to $O(\lambda)$ by

$$\Psi_0(x_1\sigma_1, x_2\sigma_2) = \frac{1}{\sqrt{2}}\phi_0(x_1)\phi_0(x_2)[\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}], \tag{15}$$

where the orbital $\phi_0(x)$ satisfies[19,20]

$$\left[-\frac{1}{2}\frac{d^2}{dx^2} - Z\delta(x) + \lambda|\phi_0(x)|^2\right]\phi_0(x) = \mu\phi_0(x). \tag{16}$$

To first order in λ,

$$\phi_0(x) = \sqrt{Z}e^{-Z|x|} + \frac{\lambda}{8\sqrt{Z}}[2e^{-3Z|x|} + e^{-Z|x|}(4Z|x| - 3)]. \tag{17}$$

The bare KS transmission amplitudes $t_s(\varepsilon)$ characterize the asymptotic behavior of the continuum states of $v_s(x) = -Z\delta(x) + \lambda|\phi_0(x)|^2$, and can be obtained to $O(\lambda)$ by a distorted-wave Born approximation (see, e.g., Ref. 21):

$$t_s = t_0 + \lambda t_1. \tag{18}$$

The result is plotted in Fig. 1, along with the interacting singlet and triplet transmission amplitudes, Eqs. (14).

We now apply Eq. (11) to show that the f_{HXC} term of Eq. (1) corrects the t_s values to their exact singlet and triplet amplitudes.

We need f_{HXC} only to $O(\lambda)$,

$$f_{\mathrm{HX}}^{\sigma\sigma'}(x,x';\omega) = \lambda\delta(x - x')(1 - \delta_{\sigma\sigma'}), \tag{19}$$

where the f_{HXC} of Eq. (1) is given to $O(\lambda)$ by $f_{\mathrm{HX}} = f_{\mathrm{H}} + f_{\mathrm{X}} = \frac{1}{4}\Sigma_{\sigma\sigma'} f_{\mathrm{HX}}^{\sigma\sigma'}$ ($=\frac{1}{2}f_{\mathrm{H}}$ here). Eq. (19) yields

$$\chi(x,x';\omega) = \chi_s(x,x';\omega) + \frac{\lambda}{2}\int dx''\chi_s(x,x'';\omega)\chi(x'',x';\omega). \tag{20}$$

Since the ground state of the N-electron system is a spin singlet, the Kronecker delta δ_{S_0,S_n} in Eq. (8) implies that only *singlet* scattering information may be extracted from χ, whereas information about triplet scattering requires the magnetic susceptibility $\mathcal{M} = \Sigma_{\sigma\sigma'}(\sigma\sigma')\chi_{\sigma\sigma'}$, related to the KS susceptibility by spin TDDFT:[22]

$$\mathcal{M}(x,x';\omega) = \chi_s(x,x';\omega) - \frac{\lambda}{2}\int dx''\chi_s(x,x'';\omega)\mathcal{M}(x'',x';\omega). \tag{21}$$

For either singlet or triplet case, since the correction to χ_s is multiplied by λ, the leading correction to $t_s(\varepsilon)$ is determined by the same quantity, $\hat{\chi}_s^{(0)} * \hat{\chi}_s^{(0)}$, where $\hat{\chi}_s^{(0)}$ is the zeroth-order approximation to the KS susceptibility [i.e., with $v_s(x) = v_s^{(0)}(x) = -Z\delta(x)$]. Its oscillatory part at large distances[23] [multiplied by $\sqrt{\rho(x)\rho(-x)}/ik$, see Eq. (11)] is equal to λt_1. We then find through Eqs. (11), (20), and (21) that

$$t_{sing} = t_s + \lambda t_1, \quad t_{trip} = t_s - \lambda t_1, \tag{22}$$

in agreement with Eqs. (14).

III. SINGLE POLE APPROXIMATION IN THE CONTINUUM

We have yet to prove an analog of Eq. (11) for Coulomb repulsion in three dimensions. But here we use quantum-defect theory[24] to deduce the result at zero energy. Consider the $l=0$ Rydberg series of bound states converging to the first ionization threshold I of the N-electron system:

$$E_n - E_0 = I - 1/[2(n - \mu_n)^2], \tag{23}$$

where μ_n is the quantum defect of the nth excited state. Let

$$\epsilon_n = -1/[2(n - \mu_{s,n})^2] \tag{24}$$

be the KS orbital energies of that series. The true transition frequencies $\omega_n = E_n - E_0$ are related through TDDFT to the KS frequencies $\omega_{s,n} = \epsilon_n - \epsilon_{\mathrm{HOMO}}$. Within the single-pole approximation (SPA) (Ref. 6):

$$\omega_n = \omega_{s,n} + 2\langle\langle \mathrm{HOMO}, n|\hat{f}_{\mathrm{HXC}}(\omega_n)|\mathrm{HOMO}, n\rangle\rangle. \tag{25}$$

Numerical studies[25] suggest that $\Delta\mu_n = \mu_n - \mu_{s,n}$ is a small number when $n \to \infty$. Expanding ω_n around $\Delta\mu_n = 0$, and using $I = -\epsilon_{\mathrm{HOMO}}$, we find

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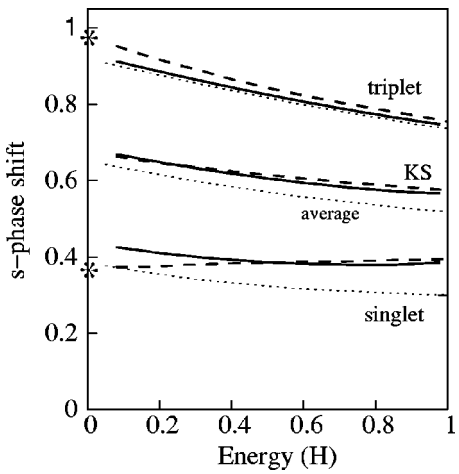

FIG. 2. *s*-phase shifts as a function of energy for electron scattering from He^+. Dashed lines: the line labeled KS corresponds to the phase shifts from the *exact* KS potential of the He atom; the other dashed lines correspond to the TDDFT singlet and triplet phase shifts calculated in the present work according to Eq. (28). Solid lines: accurate wave function calculations of electron-He^+ scattering from Ref. 28. The solid line in the center is the average of singlet and triplet phase shifts. Dotted lines: Static exchange calculations, from Ref. 29. The asterisks at zero energy correspond to extrapolating the bound→bound results of Ref. 27.

$$\omega_n = \omega_{s,n} - \Delta\mu_n/(n-\mu_{s,n})^3. \tag{26}$$

We conclude that, within the SPA,

$$\Delta\mu_n = -2(n-\mu_{s,n})^3\langle\langle \mathrm{HOMO},n|\hat{f}_{\mathrm{HXC}}(\omega_n)|\mathrm{HOMO},n\rangle\rangle. \tag{27}$$

Letting $n\to\infty$, Seaton's theorem $[\pi \lim_{n\to\infty}\mu_n = \delta(\varepsilon\to 0^+)]$ (Ref. 24) implies

$$\delta(\varepsilon) = \delta_s(\varepsilon) - 2\pi\langle\langle \mathrm{HOMO},\varepsilon|\hat{f}_{\mathrm{HXC}}(\varepsilon+I)|\mathrm{HOMO},\varepsilon\rangle\rangle, \tag{28}$$

a relation for the phase-shifts δ in terms of the KS phase-shifts δ_s applicable when $\varepsilon\to 0^+$. The factor $(n-\mu_{s,n})^3$ of Eq. (27) gets absorbed into the energy-normalization factor of the KS continuum states.

We illustrate in Fig. 2 the remarkable accuracy of Eq. (28) when applied to the case of electron scattering from He^+. For this system, an essentially exact ground-state potential for the $N=2$ electron system is known. This was found by inverting the KS equation using the ground-state density of an extremely accurate wave function calculation of the He atom.[26] We calculated the low-energy KS *s*-phase shifts from this potential, $\delta_s(\varepsilon)$ (dashed line in the center, Fig. 2), and then corrected these phase shifts according to Eq. (28) employing a hybrid approximation to f_{HXC} (Ref. 27) (= adiabatic local density approximation for antiparallel contribution to f_{HXC} and exchange-only approximation for the parallel contribution). We also plot the results of a recent highly accurate wave function calculation[28] (solid), and of static-exchange calculations[29] (dotted). The results show that phase shifts from the *N*-electron ground-state KS potential $\delta_s(\varepsilon)$ are an excellent approximation to the average of the true singlet/triplet phase shifts for an electron scattering from the $(N-1)$-electron target, just as in our one-dimensional model; they also show that TDDFT, with existing approximations, works very well to correct scattering from the KS potential to the true scattering phase shifts, at least at low energies. In fact, for the singlet phase shifts, TDDFT does better than the computationally more demanding static exchange method, and for the triplet case TDDFT does only slightly worse. Even though Eq. (28) is, strictly speaking, only applicable at zero energy (marked with asterisks in Fig. 2), it clearly provides a good description for finite (low) energies. It is remarkable that the antiparallel spin kernel, which is completely local in space and time, and whose value at each point is given by the exchange-correlation energy density of a uniform electron gas (evaluated at the ground-state density at that point), yields phase shifts for e-He^+ scattering with less than 20% error. Since a signature of density-functional methods is that, with the same functional approximations, exchange-correlation effects are often better accounted for in larger systems, the present approach holds promise as a practical method for studying large targets.

IV. CONCLUSION

To summarize, we have shown how, in one-dimension, scattering amplitudes may be obtained from TDDFT, and deduced the results for three dimensions near zero energy for Coulombic systems. The ultimate goal is to accurately treat bound-free correlation for low energy electron scattering from polyatomic molecules, with a computational cost lower than that of static exchange. An obvious limitation of the present approach is that it can only be applied to targets than bind an extra electron, and there is much work yet to be done: general proof of principle in three dimensions, testing of the accuracy of approximate ground-state KS potentials, developing and testing approximate solutions to the TDDFT Dyson-like equation, extending the methodology to cases where the anion has a sharp resonance rather than a ground state, etc.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
[4] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2000).
[5] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[6] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
[7] M. E. Casida, in *Recent Developments and Applications in Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).
[8] H. Appel, E. K. U. Gross, and K. Burke, Phys. Rev. Lett. **90**, 043005 (2003).
[9] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[10] S. Tonzani and C. H. Greene, J. Chem. Phys. **122**, 014111 (2005).
[11] G. Hanel, B. Gstir, S. Denifl, P. Scheier, M. Probst, B. Farizon, E. Illenberger, and T. D. Märk, Phys. Rev. Lett. **90**, 188104 (2003).
[12] R. K. Nesbet, Phys. Rev. A **62**, 040701(R) (2000).
[13] C. Winstead and V. McKoy, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1996), Vol. XCVI, p. 103.

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[14]M. Di Ventra and N. D. Lang, Phys. Rev. B **65**, 045402 (2002).
[15]J. Katriel and E. R. Davidson, Proc. Natl. Acad. Sci. U.S.A. **77**, 4403 (1980).
[16]M. Ernzerhof, K. Burke, and J. P. Perdew, J. Chem. Phys. **105**, 2798 (1996).
[17]C. M. Rosenthal, J. Chem. Phys. **55**, 2474 (1971).
[18]B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules* (Longman, New York, 1983).
[19]E. H. Lieb, J. P. Solovej, and J. Yngvason, Phys. Rev. Lett. **69**, 749 (1992).
[20]R. J. Magyar and K. Burke, Phys. Rev. A **70**, 032508 (2004).
[21]H. Friedrich, *Theoretical Atomic Physics* (Springer, New York, 1991), Sec. 4.1.4.
[22]M. Petersilka and E. K. U. Gross, Int. J. Quantum Chem., Quantum Chem. Symp. **30**, 1393 (1996).
[23]N. T. Maitra, A. Wasserman, and K. Burke, in *Electron Correlations and Materials Properties 2*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Kluwer Academic, Dordrecht, 2003).
[24]M. J. Seaton, Mon. Not. R. Astron. Soc. **118**, 504 (1958).
[25]A. I. Al-Sharif, R. Resta, and C. J. Umrigar, Phys. Rev. A **57**, 2466 (1998).
[26]C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).
[27]K. Burke, M. Petersilka, and E. K. U. Gross, in *Recent Advances in Density Functional Methods*, edited by P. Fantucci and A. Bencini (World Scientific, Singapore, 2000), Vol. III.
[28]A. K. Bhatia, Phys. Rev. A **66**, 064702 (2002).
[29]R. R. Lucchese and V. McKoy, Phys. Rev. A **21**, 112 (1980).

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