Electron-molecule scattering from time-dependent density functional theory

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An approach to low-energy electron-molecule scattering based on the linear response formalism of time-dependent density functional theory is given. Exact formulas to extract the transmission amplitude from the susceptibility in one-dimension are tested on a simple model. Scattering from the ground-state Kohn-Sham potential of the neutral atom can be a good approximation at low energies, as shown in electron-He+ scattering.

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The study of electron-atom and electron-molecule collisions is of pivotal importance in a variety of fields, including semiconductor plasma etching, astrochemistry, and atmospheric science [1, 2]. When the collision occurs at low energies, the calculations become especially difficult due to correlation effects between the projectile electron and those of the target [3, 4]. Several methods exist for the accurate calculation of scattering cross sections for electrons colliding with atoms or molecules [2, 5], but they share an intrinsic limitation: their computational cost grows rapidly with the number of electrons in the target, rendering them useless in practice when the wavefunction-based methods were available for the calculation of bound-state properties of molecular systems. With the advent of density functional theory (DFT) [6], computational studies of the ground-state properties of many systems became feasible for the first time.

Although correlation effects are the speciality of DFT, no rigorous theory based on DFT presently exists to study electronic scattering. Time-dependent density functional theory (TDDFT) [7] is being applied to calculate optical response, response to very intense laser fields, and even as a method for approximating non-local effects in ground-state calculations [8]. Here, we extend the application of linear response TDDFT [9] to electron-atom scattering. A generalization to the problem of electron-molecule scattering is straightforward whenever the Born-Oppenheimer approximation is valid (otherwise multicomponent DFT [10] is required). The formalism we present yields exact scattering amplitudes if two quantities, the ground-state exchange-correlation potential ($\nu_{xc}$) and the exchange-correlation kernel of TDDFT ($f_{xc}$), are known exactly.

The basic idea is simple. We want to calculate low-energy electron scattering from an N-electron target. In a classical picture, for very low energy, the projectile electron spends a long time in the neighborhood of the target, and can become fully correlated with the target electrons. We calculate the ground-state KS potential for $N+1$ electrons, e.g., the negative ion, if the target is neutral. We then apply linear-response TDDFT in a novel way to extract scattering information from the asymptotic behavior of the continuum states of the $(N+1)$-electron system, analogous to the use of R-Matrix theory [11].

Our starting point is the Dyson-like response equation that relates the susceptibility $\chi (r, r'; \omega)$ of an interacting system of ground-state density $n(r)$, with that of its ground-state Kohn-Sham analog, $\chi_s (r, r'; \omega)$ [9]. In operator form (* indicates spatial convolution):

$$\chi = \chi_s + \chi_s * f_{\text{HXC}} \ast \chi$$

(1)

We treat only systems that bind $N + 1$ electrons, so our formalism does not apply to electron scattering from many negative ions. In Eq.(1), $f_{\text{HXC}}$ is the Hartree-exchange-correlation kernel (we use atomic units throughout):

$$f_{\text{HXC}}[n](r, r'; t - t') = \frac{\delta(t - t')}{|r - r'|} + \frac{\delta v_{\text{xc}}(r, t)}{\delta n(r', t')} |_{n},$$

(2)

which is a functional of the $(N + 1)$-ground-state density $n(r)$. In Eq.(2), $v_{\text{xc}}(r, t)$ is the time-dependent exchange-correlation potential when a time-dependent perturbation is applied to the $(N + 1)$-ground state. Our prescription, proven below, is: (1) Solve the ground-state Kohn-Sham equations for the $N + 1$ system; (2) construct $\chi_s$; (3) solve Eq.(1) to obtain $\chi$; and (4) extract the scattering information at energy $\varepsilon$ from the susceptibility evaluated at a frequency $\varepsilon + I$, where $I$ is the ionization potential of the $N + 1$ system. Only the asymptotic behavior of the susceptibility is required, so step (3) doesn’t require a full solution of Eq.(1).

At this point, we limit the derivation to one-dimensional systems with finite-range interactions. Later, we present results for a real system that leave little doubt that the derivation can be generalized. Begin by writing the spin-decomposed susceptibility in the Lehman representation:

$$\chi_{\sigma\sigma'}(x, x'; \omega) = \sum_n \frac{F_{\sigma}(x) F_{\sigma'}^{*}(x')}{\omega - \Omega_n + i0^+} + cc(\omega \rightarrow -\omega),$$

(3)
with
\[ F_{n\sigma}(x) = \langle \Psi_0| \hat{n}_\sigma(x)|\Psi_n \rangle \quad ; \quad \hat{n}_\sigma(x) = \sum_{i=1}^{N+1} \delta(x - \hat{x}_i)\delta_{\sigma\sigma}, \]
(4)
where \( \Psi_0 \) is the ground-state of the \((N+1)\)-electron system, \( \Psi_n \) its \(n\)th excited state, and \( \hat{n}_\sigma(x) \) is the \(\sigma\)-spin density operator. In Eq.(3) \( \Omega_n \) is the \( \Psi_n \) transition frequency, and \( \text{"cc"} \) indicates complex conjugate. Consider now large \( x \) and \( x' \), where all the \((N+1)\)-bound states are exponentially small and the density is dominated by the decay of the highest occupied orbital. The ground-state wavefunction behaves as \[\Psi_0 \sim x \to \infty (x_2,\ldots x_{N+1}) \sqrt{\frac{n(x)}{N+1}} S_0(\sigma,\sigma_2,\ldots\sigma_{N+1}) \]
(5)
where \( \psi_0^N \) is the ground-state wavefunction of the \(N\)-electron system (the target), \( S_0 \) the spin function of the ground state and \( n(x) \) the \((N+1)\)-ground-state density. Similarly,
\[ \Psi_n \sim x \to \infty \psi_n^N(x_2,\ldots x_{N+1}) \frac{\phi_k(x)}{\sqrt{N+1}} S_0(\sigma,\sigma_2,\ldots\sigma_{N+1}) \]
(6)
where \( \psi_n^N \) is an eigenstate of the target (labeled by \( n_t \)), \( S_n \) is the spin function of the \(n\)th excited state, and \( \phi_k(x) \) is a one-electron orbital.

We restrict our attention to 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 Eq.(4), and taking into account the antisymmetry of both \( \Psi_0 \) and \( \Psi_n \), we find
\[ F_{n\sigma}(x) \to \frac{\sqrt{n(x)}\phi_k(x)}{\sqrt{N+1}} \delta_{0,nt} \times \sum_{\sigma_2,\ldots\sigma_{N+1}} S_0^*(\sigma,\ldots,\sigma_{N+1})S_n(\sigma,\ldots,\sigma_{N+1}) \]
(7)
The susceptibility at large distances is then obtained from using Eq.(7) in Eq.(3):
\[ \chi(x,x';\omega) = \sum_{\sigma,\sigma'} \chi_{\sigma\sigma'}(x,x';\omega) \to \frac{\sqrt{n(x)n(x')}}{2\pi i} \times \sum_n \phi_{kn}(x)\phi_{kn}^*(x') \delta_{0,nt} \delta_{S_0,S_n} + cc(\omega \to -\omega) \]
(8)
Since only scattering states of the \((N+1)\)-optical potential contribute to the sum in Eq.(8) at large distances, it becomes an integral over wavenumbers \( k = \sqrt{2E} \), where \( \varepsilon \) is the energy of the projectile electron:
\[ \sum_n \phi_{kn}(x)\phi_{kn}^*(x') \to \frac{1}{2\pi} \int_{0,|R|,|L|} \phi_k(x)\phi_k^*(x') dk \]
(9)
In this notation, the functions \( \phi_{kn} \) are box-normalized, and \( \phi_k(x) = \phi_k(x)/L \), where \( L \to \infty \) is the length of the box. The transition frequency \( \Omega_n = E_n^{N+1} - E_0^{N+1} \) is now simply \( \Omega_k = E_n^N + k^2/2 - E_0^{N+1} = k^2/2 + I \), where \( I \) is the first ionization potential of the \((N+1)\)-system, and \( E_0^N \) and \( E_0^M \) are the ground and \( n\)th 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:
\[ \phi_k^{[R]}(x) \to \begin{cases} e^{\pm ikx} + r_k e^{\mp ikx}, & x \to \pm \infty \\ t_k e^{\pm ikx}, & x \to \pm \infty \end{cases} \]
(10)
When \( x \to -\infty \) and \( x' = -x \) the integral of Eq.(9) is dominated by a term that oscillates in space with wavenumber \( 2\sqrt{2(\varepsilon - I)} \) and amplitude given by the transmission amplitude for spin-conserving collisions \( t_k \) at that wavenumber. Denoting this oscillatory part of \( \chi \) by \( \chi_{osc} \), we obtain:
\[ t(\varepsilon) = \lim_{x \to \infty} \left[ \frac{i\sqrt{2\varepsilon}}{\sqrt{n(x)n(-x)}} \chi_{osc}(x,-x;\varepsilon + I) \right] \]
(11)
While this formula also applies to the KS system, its transmission \( t(\varepsilon) \) can be easily obtained by solving a potential scattering problem (i.e. scattering off the \((N+1)\)-ground-state Kohn-Sham potential). The exact amplitudes \( t(\varepsilon) \) of the many-body problem are related to the \( t(\varepsilon) \) through Eqs.(11) and (1). The main result of this work is that the time-dependent response of the \((N+1)\)-electron ground-state contains the scattering information, and this is accessible via TDDFT.

We illustrate our method on a simple 1-d model of an electron scattering off a one-electron atom of nuclear charge \( Z \) [13]:
\[ \hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} - \frac{1}{2} \frac{d^2}{dx^2} - Z\delta(x_1) - Z\delta(x_2) + \lambda\delta(x_1 - x_2) \]
(12)
Electrons interact via a delta-function repulsion, scaled by \( \lambda \). With \( \lambda = 0 \) the ground state density is a simple exponential, analogous to hydrogenic atoms in 3d.

(i) Exact solution in the weak interaction limit: First, we solve for the exact transmission amplitudes to first order in \( \lambda \) using the static exchange method [14]. The total energy must be stationary with respect to variations of both the bound \( \phi_b \) and scattering \( \phi_s \) orbitals that form the spatial part of the Slater determinant: \( \phi_b(x_1)\phi_b(x_2) \pm \phi_s(x_1)\phi_s(x_1) / \sqrt{2} \), where the upper sign corresponds to the singlet, and the lower sign to the triplet case. The static-exchange equations are:
\[ \left[ -\frac{1}{2} \frac{d^2}{dx^2} + \gamma|\phi_{s,h}(x)|^2 - Z\delta(x) \right] \phi_{b,s}(x) = \mu_{b,s} \phi_{b,s}(x) \]
(13)
where \( \gamma = 2\lambda \) for the singlet, and 0 for the triplet. Thus the triplet transmission amplitude is that of a simple \( \delta \)-function:
\[ t_{trip} = t_0 = \frac{i k}{Z + i k} \]
(14)
with \( k = \sqrt{2\mu E} \). For the singlet, even though Eqs. (13) are coupled, the effect of the scattered electron on the bound electron can be neglected to first order in \( \lambda \) due to the delocalized nature of \( \phi_s \). The resulting scattering state has transmission amplitude:

\[
t_{\text{sing}} = t_0 + 2\lambda t_1, \quad t_1 = \frac{-ik^2}{(k - iz)^2(k + iz)}
\]

(ii) Our DFT solution: We now test our DFT approach to see if it can reproduce these exact results. The ground-state of the \((N + 1)\)-system \((N = 1)\) is given to first order in \( \lambda \) by:

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

where the orbital \( \phi_0(x) \) satisfies [15, 16]:

\[
-\frac{1}{2} \frac{d^2}{dx^2} - Ze^{-Z|x|} + \frac{\lambda}{8\sqrt{Z}} (2e^{-3Z|x|} + e^{-Z|x|}(4Z|x| - 3)) \phi_0(x) = \mu \phi_0(x)
\]

To first order in \( \lambda \),

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

The bare Kohn-Sham transmission amplitudes \( t_s(\varepsilon) \) characterize the asymptotic behavior of the positive-energy solutions of \( v_s(x) = -Z\delta(x) + \lambda|\phi_0(x)|^2 \), and can be obtained exactly to first order in \( \lambda \) by a distorted-wave Born approximation (see e.g. Ref.[17]):

\[
t_s = t_0 + \lambda t_1
\]

The result is plotted in Fig. 1, along with the singlet and triplet transmission amplitudes of the interacting system. We note that \( t_s \) averages the interacting triplet and singlet \( t's \) at any energy, and approaches either at both low and high energies.

We now apply Eq. (11) to show that the \( f_{\text{HXC}} \)-term of Eq. (1) corrects the \( t_s \) values to their exact singlet and triplet amplitudes. We need \( f_{\text{HXC}} \) only to first order in \( \lambda \):

\[
f_{\text{HXC}}(x, x'; \omega) = \lambda \delta(x - x')(1 - \delta_{\sigma\sigma'})
\]

where the \( f_{\text{HXC}} \) of Eq. (1) is given to first order in \( \lambda \) by

\[
f_{\text{HXC}} = f_H + f_X = \frac{3}{2} \sum_{\sigma\sigma'} f_{\text{HXC}}^{\sigma\sigma'}.
\]

For two electrons \( f_{\text{HXC}} = \frac{3}{2} f_H \). Eq. (20) yields:

\[
\chi(x, x'; \omega) = \chi_s(x, x'; \omega) + \frac{\lambda}{2} \int dx'' \chi_s(x, x''; \omega) \chi(x'', x'; \omega)
\]

Since the ground-state of the \((N + 1)\)-system is a spin-singlet, the Kronecker delta \( \delta_{S_0,S_0} \) in Eq. (8) implies that only singlet scattering information may be extracted from \( \chi \), whereas information about triplet scattering requires the magnetic susceptibility \( \mathcal{M} = \sum_{\sigma\sigma'}(\sigma\sigma')\chi_{\sigma\sigma'} \), related to the Kohn-Sham susceptibility by spin-TDDFT [18]:

\[
\mathcal{M}(x, x'; \omega) = \chi_s(x, x'; \omega) - \frac{\lambda}{2} \int dx'' \chi_s(x, x''; \omega) \mathcal{M}(x'', x'; \omega)
\]

For either singlet or triplet case, since the correction to \( \chi_s \) is already multiplied by \( \lambda \), the leading correction to \( t_s(\varepsilon) \) is determined by the same quantity, \( \chi_s^{(0)} \cdot \chi_s^{(0)} \), where \( \chi_s^{(0)} \) is the 0th order approximation to the Kohn-Sham susceptibility (i.e. with \( v_s(x) = v_s^{(0)}(x) = -Z\delta(x) \), given by [19]:

\[
\chi_s^{(0)}(x, x'; \varepsilon + I) = \sqrt{n(x)n(x')} [g^>(x, x'; \varepsilon) + g^<*(x, x'; -\varepsilon - 2I)]
\]

The outgoing Green’s function \( g^>(x, x'; \varepsilon) \) is constructed according to the prescription [20]:

\[
g^>(x, x'; \varepsilon) = -\frac{2}{W} \phi_k^{[L]}(x_<)\phi_k^{[R]}(x_>)
\]

with \( x_< \) and \( x_> \) denoting, respectively, the smaller and greater of \((x, x')\), and \( W \) being the wronskian between \( \phi_k^{[L]} \) and \( \phi_k^{[R]} \) (the scattering states of \( v_s^{(0)}(x) \)). The result when \( x \to -\infty \) and \( x' \to -x \) is:

\[
\lim_{x \to -\infty} \frac{\lambda}{2} \int dx'' \chi_s^{(0)}(x, x''; \varepsilon + I) \chi_s^{(0)}(x'', -x; \varepsilon + I) = \frac{\sqrt{n(x)n(-x)}}{i\sqrt{2\varepsilon}} (\lambda_1) e^{-2i\sqrt{2\varepsilon}x} + \text{n.o.}
\]

where “n.o” stands for non-oscillatory terms. From Eqs. (11) and (21) we find

\[
t_{\text{sing}} = t_s + \lambda t_1, \quad t_{\text{trip}} = t_s - \lambda t_1
\]

in complete agreement with Eqs. (14) and (15).
The method tested in the preceding example is applicable to any one-dimensional scattering problem. Eqs. (11) and (1) provide a way to obtain scattering information for an electron that collides with an $N$-electron target entirely from the $(N+1)$-ground-state Kohn-Sham susceptibility (and a given approximation to $f_{xc}$). A potential scattering problem is solved first from the $(N+1)$-ground-state KS potential, and the scattering amplitudes thus obtained are further corrected by $f_{xc}$ to account for e.g. polarization effects.

We conclude our results with a real case, electron scattering from the He$^+$ ion. In Fig. 2, we plot the results of a recent highly accurate wavefunction calculation [22] of the singlet and triplet $s$-phase shifts (which immediately yield the corresponding elastic scattering cross-sections). For this system, an essentially exact ground-state potential for the $N+1$ electron system is known. This was found by inverting the KS equation using the ground-state density of an extremely accurate wavefunction calculation of the He atom [21]. We calculate the low-energy Kohn-Sham $s$-phase shifts from this potential, and compare with the accurate results in Fig. 2. The results demonstrate that the $N+1$-electron ground-state KS potential is an excellent starting point for approximating bound-free correlation, and are similar to those of our one-dimensional model.

We go further, and find the TDDFT corrections to these phase-shifts. The quantum defect $\mu_{nl}$ of the bound-bound transitions (angular momentum $l$) is defined by

$$E_{nl} = -(n - \mu_{nl})^{-2}/2$$

where $E_{nl}$ is the excitation energy. As $n \to \infty$, $\mu_{nl}$ converges rapidly to a number that characterizes the zero-energy state. Seaton’s theorem [17] states

$$\delta_l(E \to 0^+) = \pi \lim_{n \to \infty} \mu_{nl},$$

where $\delta_l$ is the $l$-scattering phase shift. Thus, existing TDDFT calculations of bound-bound transitions yield zero-energy phase-shifts. The most accurate approximation to $f_{xc}$ for the He atom is a hybrid of exact exchange for parallel spin correlation and adiabatic LDA for anti-parallel correlation [23]. Extrapolating the $s$-phase quantum defect from Table 2 of Ref. [23], we find $\delta_{trip}(E = 0) = 0.97$ and $\delta_{sing}(E = 0) = 0.36$, in excellent agreement with the accurate results in Fig. 2. Thus TDDFT, with existing approximations, works very well to correct scattering from the KS potential to the true singlet and triplet scattering, at least at low energies. Work to generalize the proof to calculate scattering in 3d, and to develop a TDDFT algorithm for correcting KS scattering cross sections is ongoing.

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York, 1991), Sec. 4.1.4.


