33 Scattering Amplitudes

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33.1 Introduction

Electrons are constantly colliding with atoms and molecules: in chemical reactions, in our atmosphere, in stars, plasmas, in a molecular wire carrying a current, or when the tip of a scanning tunneling microscope injects electrons to probe a surface. 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. These *bound-free* correlations are very important. For example, it is due to bound-free correlations that ultra-slow electrons can break up RNA molecules [Hanel 2003] causing serious genotoxic damage. The accurate description of correlation effects when the targets are so complex is a major challenge. Existing approaches based on wavefunction methods, developed from the birth of quantum mechanics and perfected since then to reach great sophistication [Morrison 1983, Burke 1994, Winstead 1996], cannot overcome the exponential barrier resulting from the many-body Schrödinger equation when the number of electrons in the target is large. Wavefunction-based methods can still provide invaluable insights in such complex cases, provided powerful computers and smart tricks are employed (see, e.g., [Grandi 2004] for low-energy electron scattering from uracil), but a truly ab-initio approach circumventing the exponential barrier would be most welcome. The purpose of this chapter is to describe several results relevant to this goal.

Imagine a slow electron approaching an atom or molecule that has N electrons, and is assumed to be in its ground state, with energy E_{GS}^N. The asymptotic kinetic energy of the incoming electron is ε, so the whole system of target plus electron has a total energy of $E_{\text{GS}}^N + \varepsilon$. This is an excited state of the $(N+1)$-electron system, and, as such, it can be described by the linear response formalism of TDDFT starting from the *ground state* of the $(N+1)$-electron system. We will explain how.

The targets we will consider must be able to bind an extra electron. For example, take the target to be a positive ion, so that the $(N+1)$-electron system, with ground-state energy E_{GS}^{N+1}, is neutral. Previous chapters in this book have described how to employ TDDFT to calculate, e.g., excitation energies corresponding to bound $\rightarrow$ bound transitions from the ground state. However, in the scattering situation considered here, the excitation energy is

known in advance: it is $I + \varepsilon$, where I is the first ionization energy of the $(N + 1)$-system, $I = E_{\mathrm{GS}}^N - E_{\mathrm{GS}}^{N+1}$. It is the scattering *phase shifts*, rather than the energies, which are of interest in the scattering regime.

The TDDFT approach to scattering that we are about to discuss [Wasserman 2005b] is very different from wavefunction-based methods, yet *exact* in the sense that if the ground-state exchange-correlation potential (v_{xc}) and time-dependent exchange-correlation kernel (f_{xc}) were known exactly, we could then (in principle) calculate the *exact* scattering phase shifts for the system of $N + 1$ interacting electrons. Any given approximation to v_{xc} and f_{xc} leads in turn to definite predictions for the phase shifts. The method involves the following three steps: (i) Finding the ground-state Kohn-Sham potential of the $(N + 1)$-electron system, $v_{\mathrm{KS}}^{N+1}(\boldsymbol{r})$; (ii) Solving a *potential scattering* problem, namely, scattering from $v_{\mathrm{KS}}^{N+1}(\boldsymbol{r})$; and (iii) Correcting the Kohn-Sham scattering phase shifts towards the true ones, via linear response TDDFT.

We start by reviewing those aspects of the linear response formalism of TDDFT that were introduced in Chap. 1 and will be used in the following sections. We then derive TDDFT equations for one-dimensional scattering, and work out in detail two simple examples to show how to calculate transmission and reflection amplitudes in TDDFT. The discussion is then generalized to three dimensions, where we explain how the familiar single pole approximation for bound $\rightarrow$ bound transitions can be continued to describe bound $\rightarrow$ continuum transitions to get information about scattering states. We end with a brief summary and outlook.

33.2 Linear Response for the $(N + 1)$-Electron System

For a thorough treatment, see Chap. 1. Here we only review what will be needed for the following sections. The central equation of the linear response formalism of TDDFT is the Dyson-like response equation relating the susceptibility $\chi^{N+1}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ of a system of interacting electrons with that of its ground-state Kohn-Sham analog, $\chi_{\mathrm{KS}}^{N+1}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ [Petersilka 1996a], see (1.23). The $N + 1$ superscript was added in order to emphasize that we are going to perturb the ground-state of the $(N + 1)$-electron system, where N is the number of electrons of the target. In what follows, however, for notational simplicity, the $(N + 1)$ superscript will be dropped from all quantities. We write the spin-decomposed susceptibility in the Lehman representation:

$$\chi_{\sigma\sigma'}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \lim_{\eta \to 0^+} \left[\sum_i \frac{F_{i\sigma}(\boldsymbol{r}) F_{i\sigma'}^*(\boldsymbol{r}')}{\omega - \Omega_i + \mathrm{i}\eta^+} + \mathrm{c.c.}(\omega \to -\omega) \right], \qquad (33.1)$$

with

$$F_{i\sigma}(\boldsymbol{r}) = \langle \Psi_{\mathrm{GS}} | \hat{n}_\sigma(\boldsymbol{r}) | \Psi_i \rangle \quad ; \quad \hat{n}_\sigma(\boldsymbol{r}) = \sum_{l=1}^{N+1} \delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_l) \delta_{\sigma \hat{\sigma}_l} \qquad (33.2)$$

where Ψ_{GS} is the ground state of the $(N+1)$-electron system, Ψ_i its ith excited state, and $\hat{n}_\sigma(\boldsymbol{r})$ is the σ-spin density operator. In (33.1), Ω_i is the $\Psi_{\mathrm{GS}} \to \Psi_i$ transition frequency. The term "c.c.$(\omega \to -\omega)$" stands for the complex conjugate of the first term with ω substituted by $-\omega$. The sum in (33.1) should be understood as a sum over the discrete spectrum and an integral over the continuum. *All* excited states (labelled by i) with non-zero $F_{i\sigma}(\boldsymbol{r})$ contribute to the susceptibility. In particular, the scattering state discussed in the introduction consisting on a free electron of energy ε and an N-electron target, contributes too. How to extract from the susceptibility the scattering information about this single state? The question will be answered in the following sections, starting in one dimension.

33.3 One Dimension

33.3.1 Transmission Amplitudes from the Susceptibility

Consider large distances, where the $(N+1)$-electron ground-state density is dominated by the decay of the highest occupied Kohn-Sham orbital [Katriel 1980]; the ground-state wavefunction behaves as [Ernzerhof 1996]:

$$\Psi_{\mathrm{GS}} \xrightarrow[x\to\infty]{} \psi_{\mathrm{GS}}^N(x_2,\ldots,x_{N+1})\sqrt{\frac{n(x)}{N+1}}S_{\mathrm{GS}}(\sigma,\sigma_2,\ldots,\sigma_{N+1}) \qquad (33.3)$$

where ψ_{GS}^N is the ground-state wavefunction of the target, S_{GS} the spin function of the $(N+1)$-electron ground-state and $n(x)$ the $(N+1)$-electron ground-state density. Similarly, the asymptotic behavior of the ith excited state is:

$$\Psi_i \xrightarrow[x\to\infty]{} \psi_{i_t}^N(x_2,\ldots,x_{N+1})\frac{\phi_{k_i}(x)}{\sqrt{N+1}}S_i(\sigma,\sigma_2,\ldots,\sigma_{N+1}), \qquad (33.4)$$

where $\psi_{i_t}^N$ is an eigenstate of the target (labeled by i_t), S_i is the spin function of the ith excited state of the $(N+1)-$system, and $\phi_{k_i}(x)$ a one-electron orbital (not to be confused with φ, notation reserved for Kohn-Sham orbitals).

The contribution to $F_{i\sigma}(x)$ (33.2) from channels where the target is excited vanishes as $x \to \infty$ due to orthogonality. We therefore focus on *elastic* scattering only. Inserting (33.3) and (33.4) into the 1D-version of (33.2), and taking into account the antisymmetry of both Ψ_{GS} and Ψ_i,

$$F_{i\sigma}(x) \xrightarrow[x\to\infty]{} \sqrt{n(x)}\phi_{k_i}(x)\delta_{0,i_t} \sum_{\sigma_2\ldots\sigma_{N+1}} S_{\mathrm{GS}}^*(\sigma\ldots\sigma_{N+1})S_i(\sigma\ldots\sigma_{N+1}) \quad (33.5)$$

The susceptibility at large distances is then obtained by inserting (33.5) into the 1D-version of (33.1):

$$\chi(x, x', \omega) = \sum_{\sigma\sigma'} \chi_{\sigma\sigma'}(x, x', \omega) \xrightarrow[x,x'\to\pm\infty]{} \sqrt{n(x)n(x')}$$

$$\times \sum_i \frac{\phi_{k_i}(x)\phi_{k_i}^*(x')}{\omega - \Omega_i + \mathrm{i}\eta} \delta_{0,i_t} \delta_{S_{\mathrm{GS}},S_i} + \mathrm{c.c.}(\omega \to -\omega) \quad (33.6)$$

Since only scattering states of the $(N+1)$-electron optical potential contribute to the sum in (33.6) at large distances, it becomes an integral over wavenumbers $k = \sqrt{2\varepsilon}$, where ε is the energy of the projectile electron:

$$\sum_i \frac{\phi_{k_i}(x)\phi_{k_i}^*(x')}{\omega - \Omega_i + \mathrm{i}\eta} \xrightarrow[x,x'\to\pm\infty]{} \frac{1}{2\pi} \int_{0[\mathrm{R}],[\mathrm{L}]}^{\infty} \mathrm{d}k \, \frac{\phi_k(x)\phi_k^*(x')}{\omega - \Omega_k + \mathrm{i}\eta} \quad (33.7)$$

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

$$\phi_k^{[\mathrm{R}]}{}_{[\mathrm{L}]}(x) \to \begin{cases} \mathrm{e}^{\pm\mathrm{i}kx} + r(k)\mathrm{e}^{\mp\mathrm{i}kx}, & x \to \mp\infty \\ t(k)\mathrm{e}^{\pm\mathrm{i}kx} & , \quad x \to \pm\infty \end{cases}. \quad (33.8)$$

When $x \to -\infty$ and $x' = -x$ the integral of (33.7) is dominated by a term that oscillates in space with wavenumber $2\sqrt{k^2 - 2I}$ and amplitude given by the transmission amplitude for spin-conserving collisions $t(k)$ at that wavenumber. Denoting this by χ^{osc}, and setting $\varepsilon = \frac{1}{2}k^2$ we obtain:

$$t(\varepsilon) = \lim_{x\to-\infty} \left[\frac{\mathrm{i}\sqrt{2\varepsilon}}{\sqrt{n(x)n(-x)}} \chi^{\mathrm{osc}}(x, -x, \varepsilon + I) \right]. \quad (33.9)$$

Therefore, in order to extract the transmission amplitude $t(\varepsilon)$ from the susceptibility when an electron of energy ε collides with an N-electron target in one dimension, one should first construct the ground-state density of the $(N+1)$-electron system, perturb it in the far left with frequency $I + \varepsilon$, and then look at the oscillations of the density change in the far right: the amplitude of these oscillations ["amplified" by $\mathrm{i}\sqrt{2\varepsilon}n(x)^{-1}$] is the transmission amplitude $t(\varepsilon)$ (see Fig. 33.1).

The derivation of (33.9) does not depend on the interaction between the electrons. Therefore, the same formula applies to the Kohn-Sham system:

$$t_{\mathrm{KS}}(\varepsilon) = \lim_{x\to-\infty} \left[\frac{\mathrm{i}\sqrt{2\varepsilon}}{\sqrt{n(x)n(-x)}} \chi_{\mathrm{KS}}^{\mathrm{osc}}(x, -x, \varepsilon + I) \right]. \quad (33.10)$$

In practice, the Kohn-Sham transmission amplitudes $t_{\mathrm{KS}}(\varepsilon)$ are obtained by solving a *potential scattering* problem, i.e., scattering from the $(N+1)$-electron ground-state KS potential.
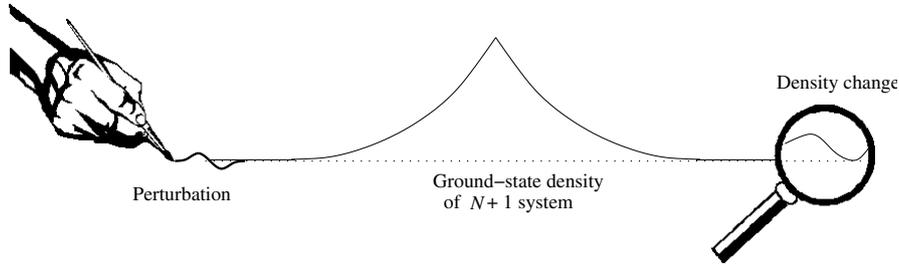
Fig. 33.1. Cartoon of (33.9). To extract the transmission amplitude for an electron of energy ε scattering from an N-electron target: apply a perturbation of frequency $\varepsilon + I$ on the far left of the $(N + 1)$-ground-state system (I is its first ionization energy), and look at how the density changes oscillate on the far right. Once amplified, the amplitude of these oscillations correspond to $t(\varepsilon)$. Reproduction from the roof of the Sistine Chapel, with permission from artist

Illustration of (33.10)

For one electron, the susceptibility is given by [Maitra 2003b]:

$$\chi_{\mathrm{KS}}(x, x', \varepsilon + I) = \sqrt{n(x)n(x')}\left[g_{\mathrm{KS}}(x, x', \varepsilon) + g_{\mathrm{KS}}^*(x, x', -\varepsilon - 2I)\right] , \quad (33.11)$$

where the Green's function $g_{\mathrm{KS}}(x, x', \varepsilon)$ has a Fourier transform satisfying

$$\left\{-\mathrm{i}\frac{\partial}{\partial t} - \frac{1}{2}\frac{\partial^2}{\partial x^2} + v_{\mathrm{KS}}(x)\right\} g_{\mathrm{KS}}(x, x', t - t') = -\mathrm{i}\delta(x - x')\delta(t - t'). \quad (33.12)$$

Let's find the transmission amplitude for an electron scattering from a double delta-function well, $v_{\mathrm{ext}}(x) = -Z_1\delta(x) - Z_2\delta(x - a)$. The Green's function can be readily obtained in this case as

$$g_{\mathrm{KS}}(x, x') = g_1(x, x') - \frac{Z_2 g_1(x, a)g_1(a, x')}{1 + Z_2 g_1(a, a)} , \quad (33.13)$$

where g_1 is the Green's function for a single delta-function of strength Z_1 at the origin. It is given by [Szabo 1989]:

$$g_1(x, x') = \frac{1}{\mathrm{i}k}\left\{\mathrm{e}^{\mathrm{i}k|x-x'|} - \frac{Z_1 \mathrm{e}^{\mathrm{i}k(|x|+|x'|)}}{\mathrm{i}k + Z_1}\right\} , \quad (33.14)$$

with $k = \sqrt{2\varepsilon}$. Having constructed χ_{KS} explicitly, application of (33.10) yields the correct answer

$$t_{\mathrm{KS}} = \frac{\mathrm{i}k/(Z_1 + \mathrm{i}k)}{1 + Z_2 g_1(a, a)} . \quad (33.15)$$

33.3.2 TDDFT Equation for Transmission Amplitudes

The exact amplitudes $t(\varepsilon)$ of the many-body problem are formally related to the $t_{KS}(\varepsilon)$ through (33.9), (33.10) and (1.23): the time-dependent response of the $(N+1)$-electron ground-state contains the scattering information, and this is accessible via TDDFT. A potential scattering problem is solved first for the $(N+1)$-electron ground-state KS potential, and the scattering amplitudes thus obtained (t_{KS}) are further corrected by f_{Hxc} to account for, e.g., polarization effects.

Even though (33.9) is impractical as a basis for computations (one can rarely obtain the susceptibility with the desired accuracy in the asymptotic regions, as we did in the previous example) it leads to practical approximations. The simplest of such approximations is obtained by iterating (1.23) once, substituting χ by χ_{KS} in the right-hand side of (1.23). This leads through (33.9) and (33.10) to the following useful distorted-wave-Born-type approximation for the transmission amplitude:

$$t(\varepsilon) = t_{KS}(\varepsilon) + \frac{1}{i\sqrt{2\varepsilon}}\langle\langle \text{HOMO}, \varepsilon | \hat{f}_{Hxc}(\varepsilon + I) | \text{HOMO}, \varepsilon \rangle\rangle . \qquad (33.16)$$

In (33.16), and from now on, the double-bracket notation stands for:

$$\langle\langle \text{HOMO}, \varepsilon | \hat{f}_{Hxc}(\varepsilon + I) | \text{HOMO}, \varepsilon \rangle\rangle =$$
$$\int \mathrm{d}x \int \mathrm{d}x' \, \varphi^*_{\text{HOMO}}(x)\varphi^{[L]*}_\varepsilon(x) f_{Hxc}(x, x', \varepsilon + I)\varphi_{\text{HOMO}}(x')\varphi^{[R]}_\varepsilon(x') , \quad (33.17)$$

where φ_{HOMO} is the highest-occupied molecular orbital of the $(N+1)$-electron system, and $\varphi^{[R]}_\varepsilon(x)$ is the energy-normalized scattering orbital of energy ε satisfying [R]-boundary conditions (see (33.8)). This is reminiscent of the single-pole approximation for excitation energies of bound $\rightarrow$ bound transitions, (1.31). Many other possibilities spring to mind for approximate solutions to (33.9).

33.3.3 A Trivial Example, $N = 0$

The method outlined above is valid for any number of particles. In particular, for the trivial case of $N = 0$ corresponding to *potential scattering*. Consider an electron scattering from a negative delta-function of strength Z in one dimension [Fig. 33.2]. The transmission amplitude as a function of ε is given by (see Sect. 2.5 of [Griffiths 1995]):

$$t(\varepsilon) = \frac{ik}{Z + ik} \quad ; \quad k = \sqrt{2\varepsilon} . \qquad (33.18)$$

How would TDDFT get this answer?: (i) Find the ground-state KS potential of the $(N+1) = 1-$electron system. The external potential admits one bound
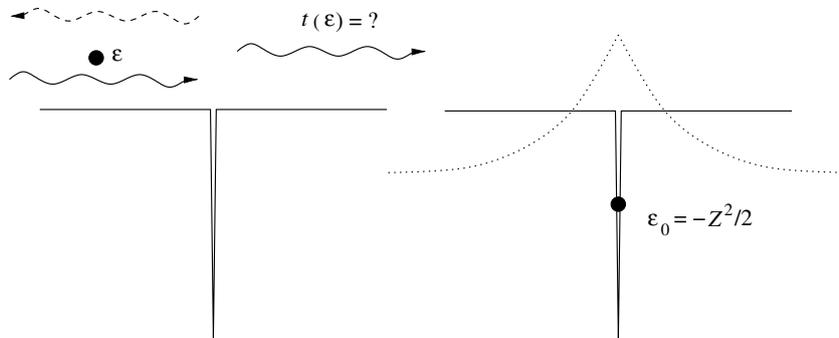
Fig. 33.2. *Left*: cartoon of an electron scattering from a negative delta-function potential. *Right*: cartoon of an electron bound to the same potential; the ground-state density decays exponentially, just as in hydrogenic ions in 3D
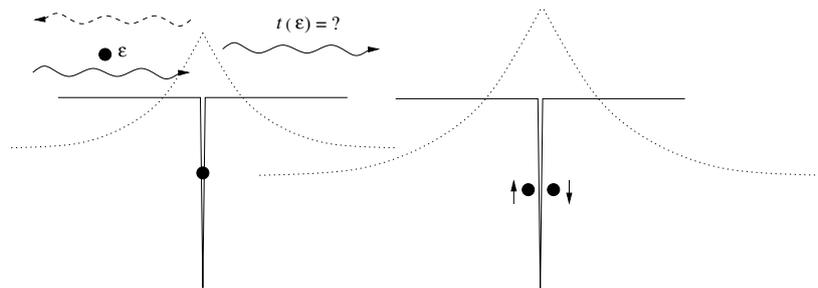
Fig. 33.3. *Left*: cartoon of an electron scattering from 1D-He$^+$. *Right*: cartoon of two electrons bound to the delta function in a singlet state

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state of energy $-Z^2/2$. The ground-state KS potential is given by $v_{\text{KS}}(x) = v_{\text{ext}}(x) + v_{\text{Hxc}}(x)$, but $v_{\text{Hxc}} = 0$ for one electron, so $v_{\text{KS}}(x) = v_{\text{ext}}(x) = -Z\delta(x)$; (ii) Solve the ground-state KS equations for positive energies, to find $t_{\text{KS}}(\varepsilon) = ik/(Z + ik)$. (iii) In this case, $f_{\text{Hxc}} = 0$, so $\chi = \chi_{\text{KS}}$, and $t = t_{\text{KS}}$. Notice that approximations that are not self-interaction corrected (to guarantee $v_{\text{Hxc}} = 0$) would give sizable errors in this simple case.

33.3.4 A Non-Trivial Example, $N = 1$

Now consider a simple 1D model of an electron scattering from a one-electron atom of nuclear charge Z [Rosenthal 1971]:

$$\hat{H} = -\frac{1}{2}\frac{\text{d}^2}{\text{d}x_1^2} - \frac{1}{2}\frac{\text{d}^2}{\text{d}x_2^2} - Z\delta(x_1) - Z\delta(x_2) + \lambda\delta(x_1 - x_2), \qquad (33.19)$$

The two electrons interact via a delta-function repulsion, scaled by λ. 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 λ using the static exchange method [Bransden 1983]. The total energy must be stationary with respect to variations of both the bound (ϕ_b) and scattering (ϕ_s) orbitals that form the spatial part of the Slater determinant: $[\phi_b(x_1)\phi_s(x_2) \pm \phi_b(x_2)\phi_s(x_1)]/\sqrt{2}$, where the upper sign corresponds to the singlet, and the lower sign to the triplet case. The static-exchange equations are:

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \gamma|\phi_{s,b}(x)|^2 - Z\delta(x) \right] \phi_{b,s}(x) = \mu_{b,s}\phi_{b,s}(x) , \qquad (33.20)$$

where $\gamma = 2\lambda$ for the singlet, and 0 for the triplet. Thus the triplet transmission amplitude is that of a simple δ-function, (33.18). This can be understood by noting that in the triplet state, the Hartree term exactly cancels the exchange (the two electrons only interact when they are at the same place, but they cannot be at the same place when they have the same spin, from Pauli's principle). The results for triplet (t_{triplet}) and singlet (t_{singet}) scattering are therefore:

$$t_{\mathrm{triplet}} = t_0 \qquad , \qquad t_0 \equiv \frac{\mathrm{i}k}{Z + \mathrm{i}k} \qquad (33.21\mathrm{a})$$

$$t_{\mathrm{singlet}} = t_0 + 2\lambda t_1 \quad , \quad t_1 \equiv \frac{-\mathrm{i}k^2}{(k - \mathrm{i}Z)^2(k + \mathrm{i}Z)} \qquad (33.21\mathrm{b})$$

(ii) *TDDFT solution:* We now show, step by step, the TDDFT procedure yielding the same result, (33.21). The first step is finding the ground-state KS potential for two electrons *bound* by the δ-function. The ground-state of the $(N + 1)$-electron system ($N = 1$) is given to $\mathcal{O}(\lambda)$ by:

$$\Psi_{\mathrm{GS}}(x_1\sigma_1, x_2\sigma_2) = \frac{1}{\sqrt{2}}\varphi_{\mathrm{GS}}(x_1)\varphi_{\mathrm{GS}}(x_2) \left[\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}\right] , \qquad (33.22)$$

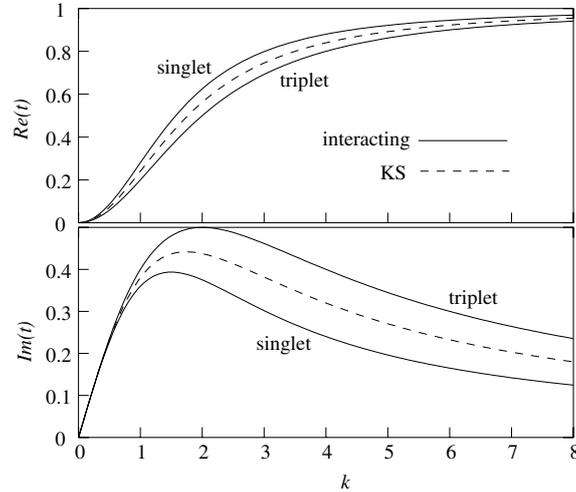where the orbital $\varphi_{\mathrm{GS}}(x)$ satisfies [Lieb 1992, Magyar 2004b]:

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z\delta(x) + \lambda|\varphi_{\mathrm{GS}}(x)|^2 \right] \varphi_{\mathrm{GS}}(x) = \mu\varphi_{\mathrm{GS}}(x) \qquad (33.23)$$

To first order in λ,

$$\varphi_{\mathrm{GS}}(x) = \sqrt{Z}e^{-Z|x|} + \frac{\lambda}{8\sqrt{Z}}\left\{ 2e^{-3Z|x|} + e^{-Z|x|}(4Z|x| - 3) \right\} . \qquad (33.24)$$

The bare KS transmission amplitudes $t_{\mathrm{KS}}(\varepsilon)$ characterize the asymptotic behavior of the continuum states of $v_{\mathrm{KS}}(x) = -Z\delta(x) + \lambda|\varphi_{\mathrm{GS}}(x)|^2$, and can be obtained to $\mathcal{O}(\lambda)$ by a distorted-wave Born approximation (see, e.g., Sect. 4.1.4 of [Friedrich 1991]):

$$t_{\mathrm{KS}} = t_0 + \lambda t_1 . \qquad (33.25)$$

Fig. 33.4. Real and imaginary parts of the KS transmission amplitude t_{KS}, and of the interacting singlet and triplet amplitudes, for the model system of (33.19). $Z = 2$ and $\lambda = 0.5$ in this plot. Reprinted with permission from [Wasserman 2005b]. Copyright 2005, American Institute of Physics

The result is plotted in Fig. 33.4, along with the interacting singlet and triplet transmission amplitudes, (33.21). The quantity λt_1 is the *error* of the ground-state calculation. The interacting problem cannot be reduced to scattering from the $(N + 1)$-KS potential, but this is certainly a good starting point; in this case, the KS transmission amplitudes are the exact average of the true singlet and triplet amplitudes [compare (33.25) with (33.21)].

We now apply (33.9) to show that the f_{Hxc}-term of (1.23) corrects the t_{KS} values to their exact singlet and triplet amplitudes. The kernel f_{Hxc} is only needed to $\mathcal{O}(\lambda)$:

$$f_{\mathrm{Hx},\,\sigma\sigma'}(x, x', \omega) = \lambda\delta(x - x')(1 - \delta_{\sigma\sigma'}), \qquad (33.26)$$

where the f_{Hxc} of (1.23) is given to $\mathcal{O}(\lambda)$ by $f_{\mathrm{Hx}} = f_{\mathrm{H}} + f_{\mathrm{x}} = \frac{1}{4}\sum_{\sigma\sigma'} f_{\mathrm{Hx},\,\sigma\sigma'}$ ($= \frac{1}{2}f_{\mathrm{H}}$ here). Equation (33.26) yields:

$$\chi(x, x', \omega) = \chi_{\mathrm{KS}}(x, x', \omega) + \frac{\lambda}{2}\int \mathrm{d}x''\, \chi_{\mathrm{KS}}(x, x'', \omega)\chi(x'', x', \omega). \qquad (33.27)$$

Since the ground state of the 2-electron system is a spin-singlet, the Kronecker delta $\delta_{S_{\mathrm{GS}}, S_i}$ in (33.6) implies that only *singlet* scattering information may be extracted from χ, whereas information about triplet scattering requires the magnetic susceptibility $\mathcal{M} = \sum_{\sigma\sigma'}(\sigma\sigma')\chi_{\sigma\sigma'}$, related to the KS susceptibility by spin-TDDFT [Petersilka 1996b]:

$$\mathcal{M}(x, x', \omega) = \chi_{\mathrm{KS}}(x, x', \omega) - \frac{\lambda}{2}\int \mathrm{d}x''\, \chi_{\mathrm{KS}}(x, x'', \omega)\mathcal{M}(x'', x', \omega). \qquad (33.28)$$

For either singlet or triplet case, since the correction to χ_{KS} is multiplied by λ, the leading correction to $t_{\text{KS}}(\varepsilon)$ is determined by the same quantity, $\hat{\chi}_{\text{KS}}^{(0)} * \hat{\chi}_{\text{KS}}^{(0)}$, where $\hat{\chi}_{\text{KS}}^{(0)}$ is the 0th order approximation to the KS susceptibility [i.e., with $v_{\text{KS}}(x) = v_{\text{KS}}^{(0)}(x) = -Z\delta(x)$]. Its oscillatory part at large distances [Maitra 2003b] [multiplied by $\sqrt{n(x)n(-x)}/ik$, see (33.9)] is precisely equal to λt_1. We then find through (33.9), (33.27), and (33.28) that

$$t_{\text{singlet}} = t_{\text{KS}} + \lambda t_1 \quad , \quad t_{\text{triplet}} = t_{\text{KS}} - \lambda t_1 \,, \tag{33.29}$$

in agreement with (33.21).

The method illustrated in the preceeding example is applicable to any one-dimensional scattering problem. Equations (33.9) and (1.23) provide a way to obtain scattering information for an electron that collides with an N-electron target *entirely* from the $(N+1)$-electron ground-state KS susceptibilty (and a given approximation to f_{xc}).

33.4 Three Dimensions

33.4.1 Single-Pole Approximation in the Continuum

We have yet to prove an analog of (33.9) for Coulomb repulsion in three dimensions. But we can use quantum-defect theory [Seaton 1958] 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 $(N+1)$-electron system:

$$E_i - E_{\text{GS}} = I - 1/\left[2(i - \mu_i)^2\right] \,, \tag{33.30}$$

where μ_i is the quantum defect of the ith excited state. Let

$$\varepsilon_i = -1/\left[2(i - \mu_{\text{KS},\,i})^2\right] \tag{33.31}$$

be the KS orbital energies of that series. The true transition frequencies $\omega_i = E_i - E_{\text{GS}}$, are related through TDDFT to the KS frequencies $\omega_{\text{KS},\,i} = \varepsilon_i - \varepsilon_{\text{HOMO}}$, where $\varepsilon_{\text{HOMO}}$ is the HOMO energy. Within the single-pole approximation (SPA) [Petersilka 1996a], applicable to Rydberg excitations according to the criteria of applicability discussed in [Appel 2003]:

$$\omega_i = \omega_{\text{KS},\,i} + 2\langle\langle \text{HOMO}, i | \hat{f}_{\text{Hxc}}(\omega_i) | \text{HOMO}, i \rangle\rangle \tag{33.32}$$

Numerical studies [Al-Sharif 1998] suggest that $\Delta\mu_i = \mu_i - \mu_{\text{KS},\,i}$ is a small number when $i \to \infty$. Expanding ω_i around $\Delta\mu_i = 0$, and using $I = -\varepsilon_{\text{HOMO}}$, we find:

$$\omega_i = \omega_{\text{KS},\,i} - \Delta\mu_i/(n - \mu_{\text{KS},\,i})^3 \,. \tag{33.33}$$

We conclude that, within the SPA,
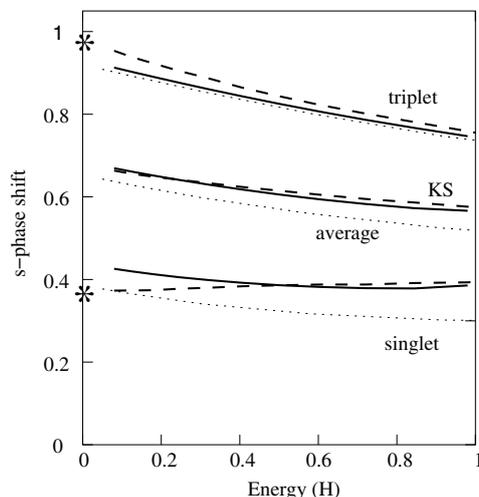
Fig. 33.5. s-phase shifts as a function of energy for electron scattering from He$^+$. *Dashed lines*: the line labeled KS corresponds to the phase shifts from the *exact* KS potential of the He atom; the other dashed lines correspond to the TDDFT singlet and triplet phase shifts calculated in the present work according to (33.35). *Solid lines*: accurate wavefunction calculations of electron-He$^+$ scattering from [Bhatia 2002]. The solid line in the center is the average of singlet and triplet phase shifts. *Dotted lines*: Static exchange calculations, from [Lucchese 1980]. The asterisks at zero energy correspond to extrapolating the bound $\rightarrow$ bound results of [Burke 2002]. Reprinted with permission from ref.[Wasserman 2005b]. Copyright 2005, American Institute of Physics

$$\Delta\mu_i = -2(i - \mu_{\mathrm{KS},\,i})^3 \langle\langle \mathrm{HOMO}, i | \hat{f}_{\mathrm{Hxc}}(\omega_i) | \mathrm{HOMO}, i \rangle\rangle. \tag{33.34}$$

Letting $i \rightarrow \infty$, Seaton's theorem $[\pi \lim_{i \rightarrow \infty} \mu_i = \delta(\varepsilon \rightarrow 0^+)]$ [Seaton 1958] implies:

$$\delta(\varepsilon) = \delta_{\mathrm{KS}}(\varepsilon) - 2\pi \langle\langle \mathrm{HOMO}, \varepsilon | \hat{f}_{\mathrm{Hxc}}(\varepsilon + I) | \mathrm{HOMO}, \varepsilon \rangle\rangle \tag{33.35}$$

a relation for the phase-shifts δ in terms of the KS phase-shifts δ_{KS} applicable when $\varepsilon \rightarrow 0^+$. The factor $(i - \mu_{\mathrm{KS},\,i})^3$ of (33.34) gets absorbed into the energy-normalization factor of the KS continuum states.

We illustrate in Fig. 33.5 the remarkable accuracy of (33.35) 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 wavefunction calculation of the He atom [Umrigar 1994]. We calculated the low-energy KS s-phase shifts from this potential, $\delta_{\mathrm{KS}}(\varepsilon)$ (dashed line in the center, Fig. 33.5), and then corrected these phase shifts according to (33.35) employing the BPG approximation to f_{Hxc} [Burke 2002] (which amounts to using the adiabatic local density approximation for the

antiparallel contribution to f_{Hxc} and exchange-only approximation for the parallel contribution). We also plot the results of a highly accurate wavefunction calculation [Bhatia 2002] (solid), and of static-exchange calculations [Lucchese 1980] (dotted). The results show that phase shifts from the $(N+1)$-electron ground-state KS potential, $\delta_{\mathrm{KS}}(\varepsilon)$, are excellent approximations to the average of the true singlet/triplet phase shifts for an electron scattering from the N-electron target, just as in the one-dimensional model of the previous section; 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 (33.35) is, strictly speaking, only applicable at zero energy (marked with asterisks in Fig. 33.5), 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.

33.4.2 Partial-Wave Analysis

For the case of spherically symmetric $(N + 1)$-electron ground states, useful expressions can be derived for the transition matrix elements (t-matrix) in the angular momentum representation. For example, the matrix elements in the usual definition [Gonis 1992] $t_l \equiv -k^{-1} \exp[-ik\delta_l] \sin \delta_l$ are given by:

$$t_l = t_l^{\mathrm{KS}} + 4\langle\langle f_{\mathrm{Hxc}}\rangle\rangle_l \quad , \tag{33.36}$$

where the t_l^{KS} are the Kohn-Sham t-matrix elements, and

$$\langle\langle f_{\mathrm{Hxc}}\rangle\rangle_l = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \frac{\varphi_{\mathrm{HOMO}}(r_1)\phi(r_2)}{(r_1 r_2)^2} f_{\mathrm{Hxc}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \varepsilon + I)\times$$
$$\times \varphi_{kl}(r_1)\phi_{kl}(r_2)\mathcal{Y}^{\hat{\boldsymbol{r}}_1\hat{\boldsymbol{r}}_2}_{l_{\mathrm{HOMO}}m_{\mathrm{HOMO}}}\mathcal{Y}^{*\hat{\boldsymbol{r}}_1\hat{\boldsymbol{r}}_2}_{l0} \quad , \quad (33.37)$$

with $\mathcal{Y}^{\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}'}_{lm} \equiv Y_l^m(\hat{\boldsymbol{r}})Y_l^{m*}(\hat{\boldsymbol{r}}')$. In (33.37), the φ's are *radial* Kohn-Sham orbitals regular at the origin, and the ϕ's are quasiparticle amplitudes determined by the asymptotic behavior of the interacting radial Green's function (see Sect. 2.3.2 of [Wasserman 2005a]). These are generally difficult to obtain in practice, but approximating them by the corresponding Kohn-Sham orbitals

yields a simple prediction for the t-matrix elements. Furthermore, the single-pole approximation of (33.35) is obtained from (33.36) after expanding it to first order in $\delta_l - \delta_l^{\mathrm{KS}}$.

33.5 Summary and Outlook

Based on the linear response formalism of TDDFT we have discussed a new way of calculating elastic scattering amplitudes for electrons scattering from targets that can bind an extra electron. In one dimension, transmission amplitudes can be extracted from the (N+1)-electron ground-state susceptibility, as indicated by (33.9). Since the susceptibility of the interacting system is determined by the Kohn-Sham susceptibility within a given approximation to the exchange-correlation kernel, the transmission amplitudes of the interacting system can be obtained by appropriately correcting the bare Kohn-Sham scattering amplitudes. Equation (33.16), reminiscent of the single-pole approximation for bound $\rightarrow$ bound transitions, provides the simplest approximation to such a correction. A similar formula for scattering phase shifts near zero energy, (33.35), was obtained in three dimensions by applying concepts of quantum defect theory.

These constitute first steps towards the ultimate goal, which is to accurately treat bound-free correlation for low-energy electron scattering from polyatomic molecules. An obvious limitation of the present approach is that it can only be applied to targets that bind an extra electron because the starting point is always the $(N + 1)$-ground-state Kohn-Sham system, which may not exist if the N-electron target is neutral, and certainly does not exist if the target is a negative ion. In addition to extending the formalism to treat such cases, there is much work yet to be done: a 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 formalism to inelastic scattering, etc. Thus, there is a long and winding road connecting the first steps presented here with the calculations of accurate cross sections for electron scattering from large targets when bound-free correlations are important. The present results show that this road is promising. Of course, "the road goes ever on and on..." [Baggins 1973] but this section looks worthwhile.

Acknowledgements