Dynamical Green's function and an exact optical potential for electron-molecule scattering including nuclear dynamics

Joachim Brand, Lorenz S. Cederbaum, and Hans-Dieter Meyer

Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

We derive a rigorous optical potential for electron-molecule scattering including the effects of nuclear dynamics by extending the common many-body Green's function approach to optical potentials beyond the fixed-nuclei limit for molecular targets. Our formalism treats the projectile electron and the nuclear motion of the target molecule on the same footing whereby the dynamical optical potential rigorously accounts for the complex many-body nature of the scattering target. One central result of the present work is that the common fixed-nuclei optical potential is a valid adiabatic approximation to the dynamical optical potential even when projectile and nuclear motion are (nonadiabatically) coupled as long as the scattering energy is well below the electronic excitation thresholds of the target. For extremely low projectile velocities, however, when the cross sections are most sensitive to the scattering potential, we expect the influences of the nuclear dynamics on the optical potential to become relevant. For these cases, a systematic way to improve the adiabatic approximation to the dynamical optical potential is presented that yields nonlocal operators with respect to the nuclear coordinates. [S1050-2947(99)02210-6]

PACS number(s): 34.80.Gs, 34.10.+x

I. INTRODUCTION

The concept of an optical potential as a physical entity that governs the scattering of a single particle by a composite target is an intuitively appealing phenomenological concept that goes back to the early days of nuclear physics. In principle, the scattering of a nonrelativistic, quantum-mechanical particle off an N-particle target is a many-body problem and governed by the $(N+1)$-particle Schrödinger equation. In the so-called optical model [1], the elastic scattering problem is alternatively described by an effective single-particle Schrödinger (or Lippmann-Schwinger) equation. All effects of the interaction of the projectile particle with the target are contained in the so-called optical potential. In general, this optical potential has to be a very complicated object: It becomes a *nonlocal* operator because exchange and rearrangement of target particles have to be considered. An *energy dependence* has to account for possible excitations of the target and if inelastic scattering is energetically possible, the optical potential is *non-Hermitian* in order to describe the loss of scattering amplitude into the inelastic channels. One major technical advantage of using optical potentials in numerical calculations is that the scattering problem can be separated from the many-body problem and the latter can be treated using bound-state techniques.

The ability of many-body theory to derive exact, though not unique, optical potentials was a great success in the 1950s [2–4]. The optical potential of Feshbach [1–3] follows from the most straightforward derivation by projection from the $(N+1)$-particle Schrödinger equation. An important alternative can be found in the self-energy of the single-particle Green's function of traditional many-body theory [4–6].

In contrast to the Green's function approach, the Feshbach optical potential is not easily amenable to perturbation theoretical approximations. Achieving a balanced and consistent treatment of ground- and excited-state correlation is thus difficult to achieve. Moreover, Mahaux and Sartor [7] have found in applications to nuclear matter that the nonlocality in the Feshbach optical potential is more complicated than in the Green's function optical potential. The numerical applications of Feshbach's theory on electron-molecule scattering reported so far have been realized by projection of configuration interaction (CI) matrices [8,9] but have rarely gone beyond the uncorrelated Hartree-Fock level for the description of the target's ground state. The inclusion of correlated, i.e., multiconfigurational, target wave functions in this context presents a delicate problem [10,11].

On the other hand, the Green's function optical potential [4] defined by the Dyson equation [12] has turned out to be well behaved and well suited for numerical calculations. The Green's function approach to the optical potential has the advantage that the self-energy of the single-particle Green's function is easily accessible through the Feynman-Dyson perturbation expansion [12]. Thus a balanced treatment of ground-state and excited-state correlation is automatically achieved. Various approximation schemes for the self-energies of molecules have been developed [13–15] and applications to electron-molecule scattering have been reported in Refs. [16–20].

All the previous calculations employing optical potentials have been done in the fixed-nuclei limit where the effects of nuclear motion are neglected altogether. A great variety of methods and numerical procedures can be used for solving the single-particle scattering equations in the fixed-nuclei limit, such as, e.g., the R-matrix [21–23], the Schwinger-variational [24], the complex-Kohn [25,26], and the close-coupling [27,28] approaches. An often-used approximate treatment of the nuclear motion derives from the Born-Oppenheimer approximation. In this so-called adiabatic-nuclei approximation [29,30,27], fixed-nuclei S-matrix elements for each configuration R of the atomic nuclei are averaged, weighted by the nuclear wave functions of the iso-

lated target molecule. This approximation, however, breaks down for low projectile energies and, in particular, for resonant vibrational excitation (see, e.g., [31]). Finally, in situations where the electronic projectiles move with velocities that are comparable to the typical velocities of nuclear motion, it becomes indispensable to treat the coupled motion correctly.

The most straightforward way of accounting for the full, nonadiabatic coupling of the nuclear motion to the motion of the projectile electron is realized in the close-coupling formalism [27,28]. In this formalism, the scattering wave function of the full problem (i.e., the degrees of freedom of $N+1$ electrons and the nuclear degrees of freedom appear as variables) is expanded in a finite set of basis functions that are chosen according to appropriate exact or approximate constants of motion. Usually it is not feasible to include excited electronic states of the target in the close-coupling expansion. These states, however, are necessary to describe polarization effects correctly. In the literature, so far model potentials void of rigorous justification have been used to account for this defect [27,32–34]. The close-coupling formalism further has the problem that the numerical calculations are difficult to converge for very low projectile energies [35].

An alternative to the one-step close-coupling expansion for treating the nuclear dynamics in electron-molecule scattering is a two-step procedure employing the so-called projection-operator (PO) formalism [36–38]. Based on the assumption of a resonance in fixed-nuclei electron scattering, the PO approach can be used to treat the nuclear dynamics going beyond the adiabatic-nuclei picture. In the PO formalism the electronic scattering problem is separated from the nuclear dynamics by Feshbach projection such that only some resonance parameters, which can be taken from fixed-nuclei scattering calculations, determine the equations for the nuclear dynamics that have to be solved. The coupling to the continuum of electronic scattering wave functions enters the nuclear dynamics via a complex, nonlocal potential. Different levels of approximation for the nonadiabatic coupling of electronic and nuclear motion are reached by local and nonlocal models for the complex potential [36]. The PO method has been very successful in explaining many features of resonant electron-molecule scattering and it gives a very intuitive picture for the mechanism of many physical processes like, e.g., resonant vibrational excitation [37]. On the other hand, it is not *per se* an exact approach because only resonant contributions to the cross sections can be treated. There are always nonresonant contributions (also called background contributions) that cannot be evaluated in the PO formalism but may actually dominate the spectra in off-resonance scattering. Sometimes no dominating resonance is present at all, and sometimes numerous resonances contribute which are difficult to identify individually. For these cases the separation of nuclear and electronic motion ultimately fails. Also the nonlocality of the complex potential usually becomes very complicated and difficult to model for very slow scattering electrons: Details of the electron-molecule interaction and the dynamical coupling of electronic, vibrational, and rotational degrees of freedom become important when the time scales of projectile and nuclear motion in the target are comparable. As an example we may mention the scattering

by a polar molecule with a supercritical or near-to-critical dipole moment. As is well known, a supercritical, nonrotating dipole ($D > 1.625$ D) can bind an excess electron but this bound state is weakened or even disappears if the dipole is allowed to rotate [39]. It is, however, very difficult to include the correct coupling of rotational degrees of freedom in the nonlocal complex potential model [40] and thus a full dynamical calculation including all relevant degrees of freedom may become necessary in order to describe the physics of very-low-energy scattering by polar molecules correctly.

To our knowledge, no one has yet given a rigorous derivation of an optical potential for the scattering electron that takes full account of the nuclear motion. To close this gap is the main objective of the present paper. In this paper we will present an optical potential that is based on the usual Green's function optical potential but allows us to treat projectile and nuclear motion on the same footing. This so-called dynamical optical potential is given by the self-energy of the dynamical Green's function, an extension of the usual single-particle Green's function including the nuclear kinetic-energy operator. The dynamical optical potential is an optical potential for electron-molecule scattering that is elastic with respect to electronic excitations of the target but inelastic with respect to the vibrations or rotations of the target. The only assumption that is used throughout this paper is that the Born-Oppenheimer approximation is valid for the target's ground state. Otherwise the dynamical optical potential is exact. It takes full account of the many-body effects of electron scattering including exchange and polarization as well as the full nonadiabatic coupling of the projectile motion to the nuclear motion of the target. The expressions we derive for the exact optical potential may provide guidance for the choice of model potentials on the one hand, and on the other hand are amenable to *ab initio* approximations and can be calculated with standard quantum-chemical methods.

This paper is organized as follows. In the next section we will start with reviewing the definition of the traditional single-particle Green's function of many-body theory. Applied only to the electronic degrees of freedom of a molecule at fixed nuclear configuration, we also call this propagator the electronic Green's function. In the subsequent Sec. II B we then define the dynamical Green's function, which allows for the treatment of the full molecular dynamics including the nuclear degrees of freedom as dynamical variables. We also define the closely related (nuclear) inelastic Green's function that shows the close relation to the recently developed theory of electronically inelastic Green's functions. Section II is closed by showing how the electronic propagator can be obtained in a suitable limit from the dynamical Green's function. In the third section an algebraic derivation of Dyson's equation for the electronic Green's function is reviewed before the dynamic Green's function is shown to fulfill a Dyson equation and the dynamical self-energy is defined. Section IV treats the relation to electron-molecule scattering. The dynamical self-energy is shown to be closely related to the optical potential for the coupled motion of the projectile electron and the atomic nuclei of the target molecule in electronically elastic scattering. Expressions for the scattering S and T matrices are shown for inelastic processes with respect to the nuclear coordinates including vibrational or rotational excitation, associative detachment, and disso-

ciative attachment. In Sec. IV B an effective Schrödinger equation using the dynamical optical potential is discussed. A direct derivation for the effective Schrödinger equation based on projection operators is given in Sec. IV C, which yields additional insight into the relation of our Green's function approach to Feshbach's theory. The well-known static-exchange and the fixed-nuclei scattering equations are identified as approximations to our exact equations in Secs. IV D 1 and IV D 2. The rest of Sec. IV D is devoted to the discussion of different possible approximations to the dynamical optical potential, in particular, concerning the treatment of the nuclear dynamics in virtual electronic excitations of the target. We also discuss how to compute the dynamical optical potential using standard *ab initio* quantum chemistry methods.

II. THE DYNAMICAL SINGLE-PARTICLE GREEN'S FUNCTION

Traditional many-body theory [12] deals with systems of indistinguishable particles. Applications to molecules usually treat only the electronic degrees of freedom in the many-body formalism and freeze the nuclear configuration. After briefly reviewing the definition of this purely electronic single-particle Green's function we will define the dynamical Green's function, which allows us to treat the nuclear degrees of freedom as dynamical variables.

A. The electronic Green's function

The usual single-particle Green's function $G(rt,r't')$ of nonrelativistic many-body theory is defined by [12]

$$iG(rt,r't') = \langle \Psi_0^N | \bar{\psi}(r,t)\bar{\psi}^\dagger(r',t') | \Psi_0^N \rangle \theta(t-t')$$
$$- \langle \Psi_0^N | \bar{\psi}^\dagger(r',t')\bar{\psi}(r,t) | \Psi_0^N \rangle \theta(t'-t). \quad (1)$$

Here, $\theta(t)$ is Heaviside's step function, $|\Psi_0^N\rangle$ denotes the exact (correlated) ground state of the N-particle system, and $\bar{\psi}^\dagger(r,t)$ is the Heisenberg field operator, which creates a particle at position r and time t. Although we consider fermionic particles, electrons, in particular, we suppress the notation of spin indices for simplicity (r may be considered as spin-space variable). In applications of many-body theory to molecular physics one usually assumes an adiabatic decoupling of electronic and nuclear motion and thus only treats the electronic degrees of freedom explicitly. $G(rt,r't')$ is then the Green's function in a system of electrons moving in the static potential of the nuclei, fixed at the coordinates R. In the following, we will call $G(rt,r't')$ the *(purely) electronic Green's function* in contrast to the later defined dynamical Green's function, which will allow us to treat nonadiabatic coupling of electronic and nuclear motion.

The Green's function decomposes into two parts, the so-called particle propagator G^+ and hole propagator G^-:

$$G(rt,r't) = G^+(rt,r't') + G^-(rt,r't'). \quad (2)$$

Noting that the (purely electronic) Heisenberg operator $\bar{\psi}^\dagger(r,t)$ evolves in time with the electronic Hamiltonian H_e,

$$\bar{\psi}^\dagger(r,t) = e^{iH_e t}\psi^\dagger(r)e^{-iH_e t}, \quad (3)$$

we can rewrite the particle and the hole propagator in the following way:

$$iG^+(rt,r't') = \langle \Psi_0^N | \psi(r)e^{-i[H_e-V_0(R)](t-t')}\psi^\dagger(r') | \Psi_0^N \rangle$$
$$\times \theta(t-t'), \quad (4)$$

$$iG^-(rt,r't') = -\langle \Psi_0^N | \psi^\dagger(r')e^{-i[V_0(R)-H_e](t-t')}\psi(r) | \Psi_0^N \rangle$$
$$\times \theta(t'-t). \quad (5)$$

Here, we made use of the fact that the electronic ground state $|\Psi_0^N\rangle$ is an eigenstate of the electronic Hamiltonian H_e with the energy of the electronic ground state $V_0(R)$:

$$H_e|\Psi_0^N\rangle = V_0(R)|\Psi_0^N\rangle. \quad (6)$$

We explicitly indicate here the dependence of V_0 on the nuclear coordinates R for later use. Of course, H_e and $|\Psi_0^N\rangle$ depend parametrically on R as well.

For convenience, we will later discuss the Green's functions mainly in the frequency instead of the time domain and using an orbital instead of a position-space representation. The corresponding expression for the electronic Green's function $G_{pq}(\omega)$, which is equivalent to the definition (1), reads

$$G_{pq}(\omega) = \left\langle \Psi_0^N \left| a_p \frac{1}{\omega - H_e + V_0(R) + i\eta} a_q^\dagger \right| \Psi_0^N \right\rangle$$
$$+ \left\langle \Psi_0^N \left| a_q^\dagger \frac{1}{\omega - V_0(R) + H_e - i\eta} a_p \right| \Psi_0^N \right\rangle. \quad (7)$$

Here, the Fourier transformation into the frequency domain is defined by $F(\omega) = \int_{-\infty}^{\infty} d(t-t')e^{i\omega(t-t')}F(t-t')$. The positive infinitesimal η remains from a convergence factor that has to be introduced to assure the convergence of the Fourier transformation. The sign of the term $i\eta$ determines the time ordering by θ functions in Eqs. (4) and (5) [12]. The transformation into the orbital representation is defined by the transformation of the creation and destruction operators of second quantization. For convenience we assume that $\{\varphi_p(r)\}_p$ is a discrete but complete set of square-integrable and normalized basis functions for the single-particle Hilbert space. The creation operator for an electron in the orbital $\varphi_p(r)$ is defined by

$$a_p^\dagger = \int dr\varphi_p(r)\psi^\dagger(r). \quad (8)$$

As usual, the orthonormality of the orbitals implies the canonical anticommutation relations $\{a_p^\dagger,a_q\} = \delta_{pq}$, etc.

The orbital set has been chosen discrete just for conceptual clearness and simple notation. The generalization to continuous sets does not pose principal problems. Convenient realizations of orbitals may be found, e.g., in the Hartree-Fock orbitals of the target (together with a convenient discretization of the continuum) or in the momentum space representation (discretized by placing the system in a finite box and employing periodic boundary conditions).

B. The dynamical Green's function

If we now want to couple the electronic motion dynamically to the nuclear motion we have to replace the electronic Hamiltonian H_e with the full molecular Hamiltonian

$$H = T_n + H_e. \tag{9}$$

It is given by the sum of the nuclear kinetic-energy operator T_n and the electronic Hamiltonian H_e. By convention, H_e contains the internuclear repulsion in addition to the electronic kinetic energy as well as the electron-nucleus Coulomb attraction and the electron-electron repulsion. The nuclear kinetic-energy operator T_n generally includes all vibrational, rotational, and translational degrees of freedom for the target molecule. For convenience we assume that the translational motion has been separated off. In this case rotation, vibration, and dissociation are the remaining degrees of freedom for the nuclear motion. In any case, T_n is a differential operator that acts on the nuclear coordinate $\boldsymbol{R}$. Thus T_n does not commute with H_e or $V_0(\boldsymbol{R})$. However, we want to assume in the following that the Born-Oppenheimer approximation is valid for the electronic ground state of the molecular target, which implies that the commutator of T_n with the electronic ground state $[T_n, |\Psi_0^N\rangle]$ is negligible. Physically, this means that the electronic configuration in $|\Psi_0^N\rangle$ depends only weakly on the nuclear coordinates.

Let us introduce the nuclear Hamiltonian

$$H_n = T_n + V_0(\boldsymbol{R}) \tag{10}$$

and let $\phi_k(\boldsymbol{R})$ be an eigenfunction with eigenvalue E_{0k}:

$$H_n \phi_k(\boldsymbol{R}) = E_{0k} \phi_k(\boldsymbol{R}). \tag{11}$$

In the following we will also use the abstract Dirac notation $|\phi_k\rangle$ from time to time for the nuclear eigenstates. The wave function $\phi_k(\boldsymbol{R})$ then emerges as the coordinate representation of the state $|\phi_k\rangle$ by $\phi_k(\boldsymbol{R}) = \langle \boldsymbol{R} | \phi_k \rangle$.

Under the assumption that T_n commutes with $|\Psi_0^N\rangle$, it is easily seen that the product wave function $|\Psi_0^N\rangle \phi_k(\boldsymbol{R})$ becomes a molecular eigenstate with energy E_{0k}:

$$H |\Psi_0^N\rangle \phi_k(\boldsymbol{R}) = E_{0k} |\Psi_0^N\rangle \phi_k(\boldsymbol{R}). \tag{12}$$

This Born-Oppenheimer picture is usually an adequate description for closed-shell molecules in the electronic ground state. The negligibility of the commutator $[T_n, |\Psi_0^N\rangle]$ is the only fundamental assumption of the theory we will develop in the following. At the end of Sec. IV C we will return to discuss the validity of this approximation and show how the theory can be generalized. At this point we want to stress that we only assume the Born-Oppenheimer picture to be valid for the nuclear dynamics in the electronic ground state of the molecule. We neither assume adiabaticity for the scattering electron nor for the electronically excited target states.

We now define the *dynamical Green's function* $\mathcal{G}(\boldsymbol{r}t, \boldsymbol{r}'t')$ as the sum of the two components for particle and hole propagation:

$$\mathcal{G}(\boldsymbol{r}t, \boldsymbol{r}'t') = \mathcal{G}^+(\boldsymbol{r}t, \boldsymbol{r}'t') + \mathcal{G}^-(\boldsymbol{r}t, \boldsymbol{r}'t'). \tag{13}$$

The particle part $\mathcal{G}^+$ is defined by

$$i\mathcal{G}^+(\boldsymbol{r}t, \boldsymbol{r}'t') = \langle \Psi_0^N | \psi(\boldsymbol{r}) e^{-i(H - E_{00})(t - t')} \psi^\dagger(\boldsymbol{r}') | \Psi_0^N \rangle$$
$$\times \theta(t - t'). \tag{14}$$

This propagator resembles the standard particle propagator (4) where the electronic Hamiltonian H_e appears instead of the total Hamiltonian H and the electronic ground-state energy $V_0(\boldsymbol{R})$ replaces the molecular ground-state energy E_{00}. Note that H now includes the nuclear kinetic energy T_n, which is a differential operator on the nuclear coordinates $\boldsymbol{R}$. Thus, $\mathcal{G}$ is also an operator on $\boldsymbol{R}$. As will be shown explicitly in Sec. IV D 4, the dynamical Green's function $\mathcal{G}$ may also be understood as a nonlocal integral operator in the nuclear coordinates:

$$\langle \boldsymbol{R} | \mathcal{G}(\boldsymbol{r}t, \boldsymbol{r}'t') | \phi \rangle = \int d\boldsymbol{R}' \mathcal{G}(\boldsymbol{r}\boldsymbol{R}t, \boldsymbol{r}'\boldsymbol{R}'t') \phi(\boldsymbol{R}'). \tag{15}$$

For the sake of simple notation, however, we will not indicate the $\boldsymbol{R}$ dependence of $\mathcal{G}$ explicitly.

The hole part $\mathcal{G}^-$ is defined with a modified Hamiltonian because this will be helpful later for the formulation of the Dyson equation:

$$i\mathcal{G}^-(\boldsymbol{r}t, \boldsymbol{r}'t')$$
$$= \langle \Psi_0^N | \psi^\dagger(\boldsymbol{r}') e^{i[H - E_{00} - 2(H_n - E_{00})](t - t')} \psi(\boldsymbol{r}) | \Psi_0^N \rangle$$
$$\times \theta(t' - t). \tag{16}$$

As long as we describe scattering or attachment processes, only $\mathcal{G}^+$ has physical significance and the propagation with the "wrong" Hamiltonian $H - E_{00} - 2(H_n - E_{00})$ does not enter the physics. If, however, we want to study ionization where the hole part carries physical significance, we have to modify the definition of the dynamical Green's function $\mathcal{G}$ and allow $\mathcal{G}^-$ to propagate with the correct Hamiltonian $H - \dot{E}_{00}$. In this case we may modify $\mathcal{G}^+$ in order to obtain a well-behaved Dyson equation. In the following we will keep to the choice (14) and (16) because we are mainly interested in the scattering problem in this paper.

Note that the particle part $\mathcal{G}^+$ can still be expressed by an expectation value of a product of Heisenberg field operators:

$$i\mathcal{G}^+(\boldsymbol{r}t, \boldsymbol{r}'t') = e^{-i(H_n - E_{00})t} \langle \Psi_0^N | \psi(\boldsymbol{r}t) \psi^\dagger(\boldsymbol{r}'t') | \Psi_0^N \rangle$$
$$\times e^{i(H_n - E_{00})t'} \theta(t - t'). \tag{17}$$

In contrast to the definition of the purely electronic single-particle Green's function (1), the field operators $\psi(\boldsymbol{r}t)$ and $\psi^\dagger(\boldsymbol{r}t')$ now evolve in time with the full molecular Hamiltonian $H = T_n + H_e$ and thus feel the effect of nuclear motion in the target. The hole part $\mathcal{G}^-$ cannot be expressed in such a simple way as $\mathcal{G}^+$.

We conclude this subsection with the expression the dynamical Green's function in the frequency domain and orbital representation:

$$\mathcal{G}_{pq}(\omega) = \left\langle \Psi_0^N \left| a_p \frac{1}{\omega - H + E_{00} + i\eta} a_q^\dagger \right| \Psi_0^N \right\rangle$$
$$+ \left\langle \Psi_0^N \left| a_q^\dagger \frac{1}{\omega - 2H_n + E_{00} + H - i\eta} a_p \right| \Psi_0^N \right\rangle. \tag{18}$$

This expression is equivalent to the definition of the dynamical Green's function in the time domain, Eqs. (13)–(16). The transformation to frequency and orbital representation is defined as before [see Eq. (7)].

C. The inelastic Green's function

The dynamical Green's function $\mathcal{G}$ presents, like the purely electronic propagator G, a matrix (or kernel of an integral operator) in time and in the coordinates of a single electron. Moreover, $\mathcal{G}$ is an operator in the nuclear coordinates $\boldsymbol{R}$. For later use and for comparison with the (electronically) inelastic theory of Ref. [41], we define the *inelastic Green's function* $\mathcal{G}^{[m,n]}$ as the matrix element of $\mathcal{G}$ with respect to the nuclear wave functions $\phi_n(\boldsymbol{R})$:

$$\mathcal{G}^{[m,n]}(\boldsymbol{r}t,\boldsymbol{r}'t') = \langle \phi_m | \mathcal{G}(\boldsymbol{r}t,\boldsymbol{r}'t') | \phi_n \rangle. \quad (19)$$

This inelastic Green's function relates directly to the S matrix of rotationally or vibrationally inelastic scattering, as we will see later.

The relation to the inelastic Green's function studied by Cederbaum [41] becomes apparent when we evaluate the particle part of $\mathcal{G}^{[m,n]}$. We introduce the symbolic notation $|0k\rangle\rangle$ for the molecular state $|\Psi_0^N\rangle\phi_k(\boldsymbol{R})$ of Eq. (12), which describes a (ro-)vibrational excitation with quantum number k in the electronic ground state. From Eqs. (11) and (17) it follows that we can write the particle part of the inelastic Green's function as

$$i\mathcal{G}^{[m,n]+}(\boldsymbol{r}t,\boldsymbol{r}'t') = \langle\langle 0m | \psi(\boldsymbol{r}t)\psi^\dagger(\boldsymbol{r}'t') | 0n \rangle\rangle$$
$$\times e^{-i[(E_{0m}-E_{00})t-(E_{0n}-E_{00})t']}\theta(t-t'), \quad (20)$$

where the double bracket notation $\langle\langle \cdot | \cdot \rangle\rangle$ indicates integration over both electronic and nuclear degrees of freedom. Expression (20) is completely analogous to the definition of Ref. [41]. While in this reference inelastic scattering between different electronic excitations of the target is considered and the nuclear degrees of freedom are neglected, the present study focuses on inelastic processes with respect to the vibrations and rotations in the same adiabatic electronic configuration. In contrast to Ref. [41] where the projectile particle, for instance a positron, is distinguishable from the target electrons, our projectile is an electron and we fully account for the indistinguishable nature of the projectile and target electrons in the present approach. For this reason we need the hole part $\mathcal{G}^-$, which, admittedly, takes on a less intuitive form than the particle part $\mathcal{G}^+$ but will prove very useful later for the formulation of the Dyson equation.

We now want to show that the dynamical Green's function $\mathcal{G}$ boils down to the usual electronic Green's function G when the nuclear dynamics becomes unimportant. Formally the transition from $\mathcal{G}$ to G is achieved by assuming that the Hamiltonian of nuclear motion $H_n = T_n + V_0(\boldsymbol{R})$ can be replaced by its lowest eigenvalue E_{00}. When we express the nuclear kinetic energy T_n in the molecular Hamiltonian $H = T_n + H_e$ by $H_n - V_0(\boldsymbol{R})$ and replace H_n by E_{00}, the parts of the dynamical Green's function $\mathcal{G}^+$ and $\mathcal{G}^-$ in Eqs. (14) and (16) reduce to the conventional expressions (4) and (5) for the electronic Green's function G^+ and G^-. Also in the inelastic formalism the transition to the purely electronic Green's function can be achieved. The elastic channel component $\mathcal{G}^{[0,0]}$ can be expressed through the purely electronic Green's function under the assumption that the nuclear kinetic energy T_n commutes with the electronic Hamiltonian H_e:

$$\mathcal{G}^{[0,0]}(\boldsymbol{r}t,\boldsymbol{r}'t') \xrightarrow{[T_n,H_e]\to 0} \int d\boldsymbol{R}\phi_0^*(\boldsymbol{R})G(\boldsymbol{r}t,\boldsymbol{r}'t')\phi_0(\boldsymbol{R}). \quad (21)$$

For the inelastic components we find an expression that reminds us of the adiabatic-nuclei approximation:

$$\mathcal{G}^{[n,m]}(\boldsymbol{r}t,\boldsymbol{r}'t') \xrightarrow{[T_n,H_e]\to 0} \int d\boldsymbol{R}e^{-i(E_{0m}-E_{00})t}\phi_n^*(\boldsymbol{R})$$
$$\times G(\boldsymbol{r}t,\boldsymbol{r}'t')\phi_m(\boldsymbol{R})e^{i(E_{0n}-E_{00})t}. \quad (22)$$

The phase factors account for the different reference energies of the channel states.

III. DYSON EQUATION AND DYNAMICAL SELF-ENERGY

In this section we will derive Dyson's equation for the dynamical Green's function and we will show that the dynamical self-energy can easily be expressed as a generalization of the purely electronic self-energy. Before turning to the dynamical Green's function, however, we will briefly review the algebraic derivation of Dyson's equation for the traditional single-particle Green's function. The Dyson equation for the dynamical Green's function will then follow easily as a generalization of this procedure.

A. The Dyson equation for the electronic Green's function

The following derivation of the Dyson equation is close in spirit to Refs. [42,43]. In the present form it has already been given in Ref. [44]. For convenience we use the representation of the Green's functions in the frequency domain and orbital representation in this section as defined by Eqs. (7) and (18).

The definition (7) of the electronic Green's function may be written in a more compact form, combining the particle and the hole propagator. To this end we introduce the following composite vectors:

$$|Y_p\rangle = \begin{pmatrix} a_p^\dagger |\Psi_0^N\rangle \\ \langle\Psi_0^N| a_p^\dagger \end{pmatrix} \quad (23)$$

and the matrix

$$\check{H} = \begin{pmatrix} H_e - V_0(\boldsymbol{R}) & 0 \\ 0 & V_0(\boldsymbol{R}) - H_e \end{pmatrix}. \quad (24)$$

We can rewrite Eq. (7) by formally expressing the single-particle Green's function as a matrix element of the resolvent of $\check{H}$ with respect to the states $|Y_p\rangle$:

$$G_{pq}(\omega) = \left\langle Y_p \left| \frac{1}{\omega - \check{H}} \right| Y_q \right\rangle. \quad (25)$$

Here, we omitted the $i\eta$ terms to avoid clumsy notation. The time ordering controlled by these terms is usually not important but may become relevant in time-dependent formulations of scattering theory (see Sec. IV A).

The scalar product of the composite vectors $|Y_p\rangle$ now includes the matrix-vector product where bras always move

to the left and kets move to the right. With respect to this canonical scalar product, the vectors $|Y_p\rangle$ fulfill the following orthonormality relation:

$$\langle Y_p | Y_q \rangle = \langle \Psi_0^N | a_p a_p^\dagger | \Psi_0^N \rangle + \langle \Psi_0^N | a_q^\dagger a_p | \Psi_0^N \rangle = \delta_{pq}.$$

When the N-electron wave function $|\Psi_0^N\rangle$ is approximated by a Slater determinant, the vector $|Y_p\rangle$ contains either a single-hole state, if p refers to an unoccupied orbital, or a single-particle state, if not. In the more general case of a correlated wave function $|\Psi_0^N\rangle$, the vectors $|Y_p\rangle$ mix $(N-1)$- and $(N+1)$-electron states. Note that in either case and for arbitrary single-particle indices p, the vectors $|Y_p\rangle$ may be seen as orthogonal states that span a linear space with the same dimension as (or isomorphous to) the single-particle Hilbert space. We will call the space spanned by the vectors $\{|Y_p\rangle\}_p$ the *primary space*. Since the primary states $|Y_p\rangle$ and their linear combinations are not, in general, exact eigenstates of the electronic Hamiltonian H_e, they couple to the higher excitations like two-particle-one-hole excitations, one-particle-two-hole excitations, etc. The space of higher excitations will be called the *secondary space* [45]. The concept of single-hole, two-particle-one-hole excitations, etc. is, of course, only adequate when the target state $|\Psi_0^N\rangle$ is dominated by a single configuration. In general, $|\Psi_0^N\rangle$ will be represented by a correlated wave function and thus the primary and the secondary space cannot be easily expressed by single-configuration basis states. For an explicit construction of a basis for the secondary space that allows for convenient approximations to the Green's function or the self-energy in the framework of the so-called intermediate state representations see Refs. [42,46]. In the following we assume that we have a basis of the composite space $\{|Q_J\rangle\}_J$ that consists of the primary states $\{|Y_p\rangle\}_p$ augmented by any suitable basis for the secondary space. The particular choice of the basis for the secondary space does not matter.

We may now proceed to derive the Dyson equation and define the self-energy setting out from Eq. (25). The basis $\{|Q_J\rangle\}_J$ of the composite space defines a basis set representation $\underline{\underline{\check{H}}}$ of the matrix Hamiltonian $\check{H}$:

$$[\underline{\underline{\check{H}}}]_{IJ} = \langle Q_I | \check{H} | Q_J \rangle. \tag{26}$$

By virtue of the subdivision of the basis set into two parts, the matrix $\underline{\underline{\check{H}}}$ is structured into blocks:

$$\underline{\underline{\check{H}}} = \begin{pmatrix} \underline{\underline{\check{H}}}_{aa} & \underline{\underline{\check{H}}}_{ab} \\ \underline{\underline{\check{H}}}_{ba} & \underline{\underline{\check{H}}}_{bb} \end{pmatrix}. \tag{27}$$

The block index a refers to primary states $\{|Y_p\rangle\}_p$ and b to the rest of the basis $\{|Q_J\rangle\}_J$. The upper left block of this matrix is readily evaluated using Eqs. (23) and (24):

$$[\underline{\underline{\check{H}}}_{aa}]_{pq} = \langle Y_p | \check{H} | Y_q \rangle = \langle \Psi_0^N | \{a_p, [\check{H}, a_q^\dagger]\} | \Psi_0^N \rangle. \tag{28}$$

It is easily seen, now, that the electronic Green's function of Eq. (25) can be understood as the upper left block of an inverse matrix:

$$\underline{\underline{G}}(\omega) = \left(\frac{1}{\omega \underline{\underline{1}} - \underline{\underline{\check{H}}}} \right)_{aa}. \tag{29}$$

The proof follows by using the completeness of the basis $\{|Q_J\rangle\}_J$ and the orthonormality of the primary states $\{|Y_p\rangle\}_p$. By simple matrix partitioning, the inverse matrix of the Green's function $\underline{\underline{G}}(\omega)$ can be expressed by

$$\underline{\underline{G}}(\omega)^{-1} = \omega \underline{\underline{1}} - \underline{\underline{\check{H}}}_{aa} - \underline{\underline{\check{H}}}_{ab} \frac{1}{\omega \underline{\underline{1}} - \underline{\underline{\check{H}}}_{bb}} \underline{\underline{\check{H}}}_{ba}. \tag{30}$$

In order to define the self-energy and to make contact to the usual form of Dyson's equation, we introduce a perturbation theoretic separation of the electronic Hamiltonian H_e into a zeroth-order part, an interaction part, and the internuclear repulsion term $U_N(\boldsymbol{R})$, which does not act as an operator on the electronic coordinates:

$$H_e = H_{e,0} + H_{e,1} + U_N(\boldsymbol{R}). \tag{31}$$

The zeroth-order part $H_{e,0}$ is a one-particle operator of the form

$$H_{e,0} = \sum_{ij} \varepsilon_{ij} a_i^\dagger a_j. \tag{32}$$

A convenient choice may be realized by the electronic kinetic energy or the Hartree-Fock operator. We do not demand the operator $H_{e,0}$ to be diagonal in the given orbital basis but a diagonalizing choice of the single-particle basis is always possible. E.g., if $H_{e,0}$ is chosen to represent the kinetic energy, the matrix $\underline{\underline{\varepsilon}}$ with the matrix elements $[\underline{\underline{\varepsilon}}]_{ij} = \varepsilon_{ij}$ becomes diagonal in the momentum representation. In atomic units, the diagonal element is then simply given by $\varepsilon_p = p^2/2$. In practical applications, $H_{e,0}$ is often chosen the Hartree-Fock operator.

On the assumption that the electronic-ground-state wave function $|\Psi_0^N\rangle$ and energy $V_0(\boldsymbol{R})$ both possess well-behaved perturbation expansions, the zeroth order of the matrix $\underline{\underline{\check{H}}}_{aa}$ can be easily evaluated from Eq. (28) to give the matrix of the zeroth-order orbital energies:

$$\underline{\underline{\check{H}}}_{aa}^{(0)} = \underline{\underline{\varepsilon}}. \tag{33}$$

It is also easy to see that the zeroth orders of the off-diagonal blocks $\underline{\underline{\check{H}}}_{ab}$ and $\underline{\underline{\check{H}}}_{ba}$ vanish and hence the zeroth-order electronic Green's function $G^{(0)}$ is found from Eq. (30) to yield

$$\underline{\underline{G}}^{(0)}(\omega) = \frac{1}{\omega \underline{\underline{1}} - \underline{\underline{\varepsilon}}}. \tag{34}$$

The electronic self-energy is defined by

$$\underline{\underline{\Sigma}}(\omega) = \underline{\underline{\check{H}}}_{aa} = \underline{\underline{\varepsilon}} + \underline{\underline{\check{H}}}_{ab} \frac{1}{\omega \underline{\underline{1}} - \underline{\underline{\check{H}}}_{bb}} \underline{\underline{\check{H}}}_{ba} \tag{35}$$

and Eq. (30) remains

$$\underline{\underline{G}}(\omega) = \frac{1}{\omega \underline{\underline{1}} - \underline{\underline{\varepsilon}} - \underline{\underline{\Sigma}}(\omega)}. \tag{36}$$

This is equivalent to the common form of Dyson's equation:

$$\underline{\underline{G}}(\omega) = \underline{\underline{G}}^{(0)}(\omega) + \underline{\underline{G}}^{(0)}(\omega) \underline{\underline{\Sigma}}(\omega) \underline{\underline{G}}(\omega). \tag{37}$$

B. The Dyson equation for the dynamical Green's function

We will show in the following that a Dyson equation for the dynamical Green's function $\mathcal{G}$ can be derived in an analogous manner, using the concepts of the preceding section. We will discuss in particular the dependence on the nuclear coordinates, which becomes important because of the introduction of the nuclear kinetic-energy operator.

Just like the electronic Green's function, the dynamical Green's function $\mathcal{G}$ of Eq. (18) can be written in a compact form combining the ionization and attachment parts. Using the composite states $|Y_p\rangle$ of Eq. (23) and the electronic matrix Hamiltonian $\breve{H}$ of Eq. (24), we can rewrite the expression (18) for the dynamical Green's function to give

$$\mathcal{G}_{pq}(\omega) = \left\langle Y_p \left| \frac{1}{\omega - \breve{H} - H_n + E_{00}} \right| Y_q \right\rangle. \quad (38)$$

We again dropped the $i\eta$ terms here for brevity. Also the 2×2 unit matrix that allows ω, H_n, and E_{00} to be applied to the two-component vector $|Y_p\rangle$ is omitted. The particularly simple and compact form of this expression can be seen as a preliminary justification for the particular choice of $\mathcal{G}^-$ in the definition (16). Dyson's equation can now easily be derived in an analogous way to the preceding section.

Comparing with the expression (25) for the electronic Green's function, we see that only the term $-H_n + E_{00}$ is additionally present in the dynamical Green's function of Eq. (38). The molecular ground-state energy E_{00} is just a constant and defines the zero point of the ω scale. The "nuclear" Hamiltonian $H_n = T_n + V_0(\boldsymbol{R})$ introduces the nuclear kinetic-energy operator T_n, which is a differential operator on the nuclear coordinates $\boldsymbol{R}$. It is therefore useful to consider the $\boldsymbol{R}$ dependence of the quantities used in the derivation of the Dyson equation.

The matrix operator $\breve{H}$ contains the electronic Hamiltonian H_e and the ground-state energy $V_0(\boldsymbol{R})$. Both quantities depend on the nuclear coordinates $\boldsymbol{R}$ and thus care has to be taken because $\breve{H}$ and H_n do not commute. For the moment we want to assume that the electronic orbital basis that defines the electronic creation operators $a_p^\dagger$ is independent of the nuclear coordinates $\boldsymbol{R}$. This is the case, e.g., for the momentum or position-space representation. This restriction is just convenient for the derivation of the Dyson equation but not essential and we will see later (Sec. IV C) that it can be lifted as long as the chosen single-particle basis for the electrons is complete. The $\boldsymbol{R}$ dependence of the composite states $|Y_p\rangle$ of Eq. (23) now derives entirely from the electronic ground state $|\Psi_0^N\rangle$. As we already mentioned in Sec. II B, we assume that the Born-Oppenheimer approximation is valid for the electronic ground state and thus the nuclear kinetic energy T_n commutes with $|\Psi_0^N\rangle$. Consequently we may assume that the nuclear Hamiltonian H_n commutes with the composite states $|Y_p\rangle$. We also assume that the basis states $|Q_J\rangle$ of the secondary space are conveniently chosen, such that the commutator with T_n or H_n can be neglected. An appropriate choice is always possible [47]. The nuclear Hamiltonian H_n can consequently be pulled out of any matrix element involving the basis states of the composite electronic space and thus the matrix representation of H_n in this basis is proportional to the unit matrix:

$$\langle Q_I | H_n | Q_J \rangle = \delta_{IJ} H_n. \quad (39)$$

In analogy to Eq. (29) we can understand the dynamical Green's function $\mathcal{G}$ as the upper left block of an inverse matrix:

$$\underline{\underline{\mathcal{G}}}(\omega) = \left(\frac{1}{(\omega - H_n + E_{00})\underline{\underline{1}} - \underline{\underline{\breve{H}}}} \right)_{aa}. \quad (40)$$

The elements of this matrix are now operators acting on the nuclear coordinates. Matrix partitioning can be applied and is completely analogous to the case of the electronic Green's function.

Owing to the partitioning (31) of the electronic Hamiltonian H_e into a zeroth-order and interaction part, we find for the zeroth-order dynamical Green's function

$$\underline{\underline{\mathcal{G}}}^{(0)}(\omega) = \frac{1}{(\omega - H_n + E_{00})\underline{\underline{1}} - \underline{\underline{\varepsilon}}}, \quad (41)$$

where $\underline{\underline{\varepsilon}}$ is again the matrix of zeroth-order single-electron energies. In the simple case where the electronic kinetic energy is chosen as the zeroth-order electronic Hamiltonian $H_{e,0}$, the matrix $\underline{\underline{\varepsilon}}$ is diagonal in the momentum representation and independent of the nuclear coordinates $\boldsymbol{R}$ as mentioned in Sec. III A. The zeroth-order dynamical Green's function $\mathcal{G}^{(0)}$ now is also diagonal and describes the simultaneous motion of a free electron and the vibrations (or rotations) of the isolated target molecule.

In the more general case where the matrix $\underline{\underline{\varepsilon}}$ depends on $\boldsymbol{R}$ (if, e.g., $H_{e,0}$ is chosen the $\boldsymbol{R}$-dependent Hartree-Fock operator), the zeroth-order propagator $\mathcal{G}^{(0)}$ may be understood to describe the coupled motion of a vibrating (or rotating) molecule in the electronic ground state and a single electron that moves under the influence of $\boldsymbol{R}$-dependent mean fields. Since the zeroth-order electronic Hamiltonian $H_{e,0}$ is a one-particle operator, the motion of the scattering electron is decoupled from the target electrons. The effective Hamiltonian for the coupled projectile and nuclear motion is thus independent of the scattering energy and simply given by $H_n + H_{e,0} - E_{00}$. The zeroth-order Green's function $\mathcal{G}^{(0)}$ is the resolvent of this effective Hamiltonian.

For the full dynamical Green's function we find

$$\underline{\underline{\mathcal{G}}}(\omega) = \frac{1}{(\omega - H_n + E_{00})\underline{\underline{1}} - \underline{\underline{\varepsilon}} - \underline{\underline{\mathcal{A}}}(\omega)}, \quad (42)$$

where the dynamical self-energy $\mathcal{A}$ is defined by

$$\underline{\underline{\mathcal{A}}}(\omega) = \underline{\underline{\breve{H}}}_{aa} - \underline{\underline{\varepsilon}} + \underline{\underline{\breve{H}}}_{ab} \frac{1}{(\omega - H_n + E_{00})\underline{\underline{1}} - \underline{\underline{\breve{H}}}_{bb}} \underline{\underline{\breve{H}}}_{ba}. \quad (43)$$

In comparison to the zeroth-order case, the dynamical self-energy $\mathcal{A}(\omega)$ now accounts for the many-body nature of the molecular target. We will demonstrate in the next section

that $\mathcal{A}(\omega)$ indeed is an optical potential for (electronically elastic) electron-molecule scattering. It is remarkable that the nuclear Hamiltonian H_n appears in the self-energy $\mathcal{A}(\omega)$ together with the ω dependence and thus introduces derivatives with respect to the nuclear coordinates. As we shall see in detail later, the dynamical self-energy thus becomes a non-local operator not only in the electronic but also in the nuclear coordinates. In Sec. IV D we will discuss the meaning of the nuclear Hamiltonian appearing in the dynamical self-energy and possible approximations.

In a very formal manner, $\mathcal{A}(\omega)$ can be expressed by the usual electronic self-energy $\Sigma(\omega)$:

$$\underline{\underline{\mathcal{A}}}(\omega) = \underline{\underline{\Sigma}}(\omega - H_n + E_{00}). \tag{44}$$

Before we turn to the discussion of the scattering S matrix and the optical potential in the next section, we would like to present the Dyson equation in terms of the inelastic Green's function $\mathcal{G}^{[m,n]}$ of Eq. (19). Carrying on the analogy to the inelastic formalism of Ref. [41] will help us in the next section to identify the dynamical self-energy with the optical potential. The inelastic formalism also yields a slightly different view of the Dyson equation as the introduction of nuclear eigenfunctions $\phi_n(\mathbf{R})$ formally leads to an equal treatment of the electronic and nuclear degrees of freedom, at the cost of having to introduce another sort of matrix indices.

Instead of using the purely electronic basis $\{|Q_J\rangle\}_J$, we introduce the product basis $\{|Q_J\rangle \otimes |\phi_n\rangle\}_{J,n}$, where $|\phi_n\rangle$ is the abstract notation for the nuclear wave function $\phi_n(\mathbf{R})$. The expression (19) for the inelastic Green's function in the frequency domain and orbital representation then reads

$$\mathcal{G}^{[m,n]}(\omega) = \left\langle \phi_m \left| \left\langle Y_p \left| \frac{1}{\omega - \breve{H} - H_n + E_{00}} \right| Y_q \right\rangle \right| \phi_n \right\rangle. \tag{45}$$

The bracket of the nuclear states $\langle \phi_m | \cdots | \phi_n \rangle$ implies integration over the nuclear coordinates. The derivation of the Dyson equation can now be redone using the matrix representation defined by the product basis. In the following we denote matrices in the labels of the nuclear states n,m by boldface letters and matrices in the electronic state labels I,J,p,q with double underbars. The zeroth-order inelastic Green's function becomes

$$\underline{\underline{\mathcal{G}}}^{(0)}(\omega) = \frac{1}{(\omega + E_{00})\underline{\underline{\mathbf{1}}} - H_n\underline{\underline{\mathbf{1}}} - \underline{\underline{\varepsilon}}}. \tag{46}$$

The matrix of the nuclear Hamiltonian H_n is diagonal due to the particular choice of the nuclear wave function basis:

$$[H_n]^{[m,n]} = \delta_{mn} E_{0n}. \tag{47}$$

The full inelastic Green's function reads

$$\underline{\underline{\mathcal{G}}}(\omega) = \frac{1}{(\omega + E_{00})\underline{\underline{\mathbf{1}}} - H_n\underline{\underline{\mathbf{1}}} - \underline{\underline{\varepsilon}} - \underline{\underline{\mathcal{A}}}(\omega)}, \tag{48}$$

where the inelastic self-energy $\underline{\underline{\mathcal{A}}}(\omega)$ is defined by

$$\underline{\underline{\mathcal{A}}}(\omega) = \underline{\underline{\breve{H}}}_{aa} - \underline{\underline{\varepsilon}} + \underline{\underline{\breve{H}}}_{ab} \frac{1}{(\omega + E_{00})\underline{\underline{\mathbf{1}}} - H_n\underline{\underline{\mathbf{1}}} - \underline{\underline{\breve{H}}}_{bb}} \underline{\underline{\breve{H}}}_{ba}. \tag{49}$$

Of course, matrix inversion and multiplication now have to include both sorts of matrix indices. The Dyson equation for the inelastic Green's function can be written as

$$\underline{\underline{\mathcal{G}}}(\omega) = \underline{\underline{\mathcal{G}}}^{(0)}(\omega) + \underline{\underline{G}}^{(0)}(\omega)\underline{\underline{\mathcal{A}}}(\omega)\underline{\underline{\mathcal{G}}}(\omega). \tag{50}$$

Note that the inelastic self-energy $\mathcal{A}$ is merely another representation of the dynamical self-energy $\mathcal{A}$. The relation is given by

$$\mathcal{A}_{pq}^{[m,n]}(\omega) = \langle \phi_m | \mathcal{A}_{pq}(\omega) | \phi_n \rangle. \tag{51}$$

IV. APPLICATION TO ELECTRON-MOLECULE SCATTERING

In this section we discuss the relation of the dynamical Green's function to the process of electron-molecule scattering. We introduce the S and T matrices of electronically elastic but vibrationally or rotationally inelastic scattering and show how they can be calculated using the dynamical Green's function formalism developed in the previous sections. We present an effective Schrödinger equation and discuss the role of the dynamical self-energy as an optical potential for the scattering process. A direct derivation of the effective Schrödinger equation is given and possible approximations to the exact equations are discussed.

A. The S and T matrices of inelastic scattering

The relation of the dynamical Green's function to the S and T matrices of scattering theory is very similar to elastic electronic scattering off atoms or rigid molecules [5,6] and completely analogous to the electronically inelastic case [41]. We therefore sketch the derivation only very briefly.

The S matrix for the processes we consider reads

$$S(p'm \leftarrow pn) = \langle\langle \Psi_{p'}^{m-} | \Psi_p^{n+} \rangle\rangle, \tag{52}$$

where the stationary scattering states $|\Psi_p^{m\pm}\rangle\rangle$ with incoming $(-)$ or outgoing $(+)$ boundary conditions are defined by

$$|\Psi_p^{n\pm}\rangle\rangle = \lim_{t \to \mp\infty} e^{-i(\varepsilon_p + E_{0n} - H)t} a_p^\dagger |\Psi_0^N\rangle |\phi_n\rangle, \tag{53}$$

and the double bracket notation again implies integration over electronic and nuclear degrees of freedom. The asymptotic states thus feature a free electron with momentum p and energy $\varepsilon_p = p^2/2$ (in atomic units) and an N-electron molecular state $|\Psi_0^N\rangle |\phi_n\rangle$ with the nth excited vibration or rotation in the electronic ground state with energy E_{0n}. For definiteness we choose the electronic kinetic energy as the zeroth-order electronic Hamiltonian $H_{e,0}$ in this section, describing the motion of free electrons. Note that the scalar product of Eq. (52) implies integration over all coordinates of the $N+1$ electrons in addition to the integration over the nuclear coordinates $\mathbf{R}$.

The S matrix can be expressed by the particle part of the inelastic Green's function of Eq. (19) in the momentum representation as follows from the definition (14) and Eqs. (52) and (53):

$$S(p'm \leftarrow pn) = \lim_{\substack{t \to +\infty \\ t' \to -\infty}} e^{i(\varepsilon_{p'} + E_{0m} - E_{00})t}$$
$$\times \mathcal{G}_{p'p}^{[m,n]+}(t,t') e^{-i(\varepsilon_p + E_{0n} - E_{00})t'}. \quad (54)$$

The particle part $\mathcal{G}^{[m,n]+}$ may be replaced here by the full Green's function $\mathcal{G}^{[m,n]}$ for two reasons.

(1) The hole part $\mathcal{G}^{[m,n]-}$ does not contribute because the S matrix only contains information about the asymptotic region of scattering where $\mathcal{G}^{[m,n]-}$ vanishes because $a_p|\Psi_0^N\rangle$ vanishes. For the effective single-particle scattering equations we are going to derive in the following, this means that ensuring the correct outgoing boundary condition avoids contamination of the wave function by unphysical contributions.

(2) The hole part $\mathcal{G}^{[m,n]-}$ does not contribute in the considered time limit because of the θ functions that appear explicitly in Eqs. (14) and (16). Therefore the particle part may be replaced by the full Green's function when the time ordering is treated properly.

We now introduce the *inelastic improper self-energy* $\underline{\underline{\mathcal{T}}}(\omega)$ in analogy to the common improper or reducible self-energy [12,6] by rewriting Eq. (50) as usual by

$$\underline{\underline{\mathcal{G}}}(\omega) = \underline{\underline{\mathcal{G}}}^{(0)}(\omega) + \underline{\underline{\mathcal{G}}}^{(0)}(\omega)\underline{\underline{\mathcal{T}}}(\omega)\underline{\underline{\mathcal{G}}}^{(0)}(\omega), \quad (55)$$

$$\underline{\underline{\mathcal{T}}}(\omega) = \underline{\underline{\mathcal{A}}}(\omega) + \underline{\underline{\mathcal{A}}}(\omega)\underline{\underline{\mathcal{G}}}^{(0)}(\omega)\underline{\underline{\mathcal{T}}}(\omega). \quad (56)$$

Following the derivations of Refs. [6,41] we can express the scattering S matrix by the improper self-energy:

$$S(p'm \leftarrow pn) = \delta_{nm}\delta_{pp'} - 2\pi i T_{p'p}^{[m,n]}(\varepsilon_p + E_{0n})$$
$$\times \delta(\varepsilon_{p'} + E_{0m} - \varepsilon_p - E_{0n}). \quad (57)$$

The inelastic improper self-energy $\mathcal{T}^{[m,n]}$ at the scattering energy $\varepsilon_p + E_{0n}$ can thus be identified with the on-shell T matrix of scattering theory. Following standard scattering theory, we see from Eq. (56) that the inelastic self-energy $\mathcal{A}^{[m,n]}(\omega)$ [or equivalently the dynamical self-energy $\mathcal{A}(\omega)$] presents the (optical) potential for the scattering process. $\mathcal{A}^{[m,n]}$ is the optical potential for multichannel scattering where the channels are defined by the eigenstates $|\phi_n\rangle$ of the nuclear motion.

The relation of the inelastic improper self-energy $\mathcal{T}$ to the improper self-energy T of the usual (electronic) single-particle Green's function ([12,6], see also [48] for explicit expressions that can be useful in the present context) can be described, in analogy to Eq. (44), by

$$\underline{\underline{\mathcal{T}}}^{[m,n]}(\omega) = \langle \phi_m | \underline{\underline{T}}(\omega - H_n + E_{00}) | \phi_n \rangle. \quad (58)$$

Note that this formal expression in fact expresses a rather complicated relation of the purely electronic improper self-energy $\underline{\underline{T}}(\omega)$ and the inelastic scattering T matrix because the nuclear kinetic energy in H_n formally appears as an energy variable of $\underline{\underline{T}}(\omega)$, which has itself a complicated dependence on the nuclear coordinates $\mathbf{R}$. If, however, T_n is omitted in this expression replacing H_n by $V_0(R)$, we can

recover the well-known adiabatic-nuclei approximation (AN) of electron-molecule scattering:

$$\mathcal{T}_{p'p}^{[m,n](AN)}(\omega) = \langle \phi_m | T_{p'p}[\omega - V_0(\mathbf{R}) + E_{00}] | \phi_n \rangle. \quad (59)$$

B. An effective Schrödinger equation

In the preceding section we identified the inelastic self-energy $\mathcal{A}^{[m,n]}$ with the optical potential for multichannel scattering. Consequently, effective one-particle equations of the Lippmann-Schwinger or Schrödinger type can be derived. In the multichannel picture one obtains sets of coupled equations, one for each combination of initial and final channel. Instead of rederiving these equations, which can be found in Ref. [41] for the analogous case of electronically inelastic scattering, we will discuss directly the time-independent Schrödinger equation in the position-space representation.

Any effective one-particle equation must involve explicitly the coordinates of the scattering electron and the labels of the nuclear states or, equivalently, the nuclear coordinates $\mathbf{R}$. Instead of the full scattering wave function

$$|\Psi_p^{n+}(\mathbf{R})\rangle = \langle \mathbf{R} | \Psi_p^{n+} \rangle$$
$$= \lim_{t \to -\infty} e^{-i(\varepsilon_p + E_{0n} - H)t} a_p^\dagger |\Psi_0^N\rangle \phi_n(\mathbf{R}), \quad (60)$$

which is the nuclear-coordinate representation of the scattering wave function of Eq. (53) and presents a wave function in the nuclear coordinates and an abstract ket in the $(N+1)$-particle space, we introduce the effective or optical wave function $f(\mathbf{r},\mathbf{R})$ by

$$f_p^{[n]+}(\mathbf{r},\mathbf{R}) = \langle \Psi_0^N | \psi(\mathbf{r}) | \Psi_p^{n+}(\mathbf{R}) \rangle. \quad (61)$$

This function can be calculated from the dynamical Green's function $\mathcal{G}$ of Eq. (13) by

$$f_p^{[n]+}(\mathbf{r},\mathbf{R}) = \lim_{t' \to \infty} \int d\mathbf{r}' \langle \mathbf{R} | \mathcal{G}(\mathbf{r},0;\mathbf{r}',t') | \phi_n \rangle$$
$$\times \varphi_p(\mathbf{r}') e^{-i(\varepsilon_p + E_{0n} - E_{00})}, \quad (62)$$

where $\varphi_p(\mathbf{r})$ is a plane wave. The relation to the scattering S matrix is given by [5,41]

$$S(p'm \leftarrow pn) = \int d\mathbf{R} \int d\mathbf{r} \phi_m^*(\mathbf{R}) \varphi_{p'}^*(\mathbf{r}) f_p^{[n]+}(\mathbf{r},\mathbf{R}). \quad (63)$$

An effective Schrödinger equation for the considered scattering problem reads

$$[H_{e,0} + H_n + \mathcal{A}(E) - E_{00}] f_p^{[n]+}(\mathbf{r},\mathbf{R}) = E f_p^{[n]+}(\mathbf{r},\mathbf{R}), \quad (64)$$

as follows by analogy from Refs. [41,5,6]. A self-contained derivation of this equation using projection operators will also be given in Sec. IV C. In the effective Schrödinger equation (64), E denotes the total energy with respect to the zero point defined at the molecular ground-state energy E_{00}. This zero point is related to a situation where the scattering electron is so far away that it does not feel any forces exerted by the target, which is in its ground state, and the particle as

well as the projectile are at rest. The zeroth-order electronic Hamiltonian $H_{e,0}$ is an operator acting only on the coordinates r of the scattering electron. According to the choice of Sec. IV A, it consists of the electronic kinetic energy and describes the motion of a free electron. Equation (64), however, is also valid if the Hartree-Fock operator is chosen as the zeroth order. In this case, $H_{e,0}$ contains also the static-exchange potential of the target molecule. The nuclear Hamiltonian H_n acts only on the nuclear coordinates R and describes the nuclear motion of the target molecule in its electronic-ground-state potential $V_0(R)$. The dynamical self-energy $\mathcal{A}(E)$ of Eqs. (43) and (44) appears here in the coordinate-space representation and takes account of the complex many-body nature of the molecular target. It acts as a nonlocal (integral) operator in the electron coordinates r and also in the nuclear coordinates R:

$$\mathcal{A}(E)f(r,R) = \int dR' \int dr' \, \mathcal{A}(r,R,r',R',E)f(r',R'). \quad (65)$$

Introducing the operator

$$\mathcal{L}(E) = H_{e,0} + H_n + \mathcal{A}(E) - E_{00}, \quad (66)$$

which can be seen as an analog of the Layzer operator [49] of the usual single-particle Green's function, the effective Schrödinger equation (64) can be written as

$$\mathcal{L}(E)f(r,R) = Ef(r,R). \quad (67)$$

This is formally a pseudoeigenvalue equation because the eigenvalue E also determines the operator $\mathcal{L}(E)$. In the scattering regime ($E > 0$) there is, of course, a solution for every E and the problem of solving Eq. (67) is to find a wave function $f(r,R)$ with the correct boundary conditions such that the equation is fulfilled at a given scattering energy E. We usually identify the dynamical self-energy $\mathcal{A}(E)$ with the dynamical optical potential although $\mathcal{A}(E)$ is not the only non-kinetic-energy component of $\mathcal{L}(E)$.

As it stands, the effective Schrödinger equation (64) or (67) is an exact equation but, of course, approximations have to be introduced in most cases to determine the integro-differential operator $\mathcal{L}(E)$. We will discuss some possibilities in Sec. IV D. The best strategy to solve Eq. (64) then certainly depends on the level of approximation introduced in the determination of $\mathcal{L}(E)$ and on the nature of the problem to be solved. A variety of methods is available. For example, close-coupling [27,28] or the other methods mentioned in Sec. I can be used to solve Eq. (64) directly for the scattering wave functions. Resonances may also be calculated using bound-state techniques by employing the complex-rotation method [50,51], complex absorbing potentials [52–54], or the stabilization method [55], etc. If necessary, the eigenvalues E may be found by iteration. Any other standard method for solving scattering problems will also do, since the corresponding Lippmann-Schwinger or effective time-dependent Schrödinger equation may also be used as starting points.

C. A direct derivation of the scattering equations

We will now show how to derive the effective Schrödinger equation (64) directly from the Schrödinger equation

for the full scattering problem, which comprises the motion of $N+1$ electrons and the nuclear motion. This derivation is fully equivalent to the derivation sketched in Sec. IV A. Although the dynamical Green's function and its Dyson equation do not appear explicitly, the direct derivation, which uses projection operators in a composite Hilbert space with particle and hole states, is firmly based on Green's function theory and has to be seen as the result of recent developments in this area [42,43]. While traditional many-body Green's function theory supplies powerful methods to compute the dynamical optical potential approximatively (see Sec. IV D), the projection-operator formulation of Dyson's equation (43) yields a complementary way of reflecting on the Green's function approach and its relation to Feshbach projection. Reconsidering in this section the algebra of Sec. III will help us to further clarify the role of an R dependence in the electronic single-particle basis and in the electronic ground state $|\Psi_0^N\rangle$. We will also have an opportunity to discuss the role of unphysical contaminations of the optical wave function.

We start from the time-independent Schrödinger equation for the full scattering problem of $N+1$ electrons and the atomic nuclei:

$$(H - E_{00})|\Psi_{\text{tot}}(R)\rangle = E|\Psi_{\text{tot}}(R)\rangle. \quad (68)$$

The total wave function $|\Psi_{\text{tot}}(R)\rangle$ is an arbitrary solution of the Schrödinger equation like, e.g., the scattering wave function $|\Psi_p^{n+}(R)\rangle$ of Eq. (60). The eigenvalue E measures the energy of the scattering system relative to the molecular ground-state energy E_{00}. Following Eq. (9), we split the total Hamiltonian H into the electronic part H_e and the nuclear kinetic energy T_n. Adding and subtracting the ground-state potential $V_0(R)$ and introducing the nuclear Hamiltonian $H_n = T_n + V_0(R)$ of Eq. (10), we may write

$$[H_e - V_0(R) + H_n - E_{00}]|\Psi_{\text{tot}}(R)\rangle = E|\Psi_{\text{tot}}(R)\rangle. \quad (69)$$

By introducing the 2×2 matrix operator $\breve{H}$ of Eq. (24) we may rewrite Eq. (69) into the two-component equation

$$[\breve{H} + (H_n - E_{00})\underline{1}_2]\begin{pmatrix} |\Psi_{\text{tot}}(R)\rangle \\ 0 \end{pmatrix} = E\begin{pmatrix} |\Psi_{\text{tot}}(R)\rangle \\ 0 \end{pmatrix}, \quad (70)$$

where $\underline{1}_2$ is the 2×2 unit matrix. Since the second component of the vector $(|\Psi_{\text{tot}}(R)\rangle, 0)^t$ is set to zero, Eq. (70) is completely equivalent to the initial Schrödinger equation (68). However, the vector $(|\Psi_{\text{tot}}(R)\rangle, 0)^t$ may also be seen as an element of the composite Y space of Ref. [45]. We now introduce the projection operator

$$P = \sum_q |Y_q\rangle\langle Y_q|, \quad (71)$$

projecting onto the primary space, which is spanned by the vectors $\{|Y_p\rangle\}$ of Eq. (23). By definition, the projector P primarily acts on the electronic degrees of freedom. However, we also have to consider the dependence on the nuclear coordinates R because the nuclear kinetic energy T_n contained in the nuclear Hamiltonian H_n introduces derivatives with respect to R into Eq. (70). The nuclear-coordinate dependence of P derives directly from the electronic ground

state $|\Psi_0^N\rangle$, as can be seen from the definition (23) of $|Y_p\rangle$ when we assume that the basis of single-particle orbitals $\varphi_p(\mathbf{r})$ is independent of $\mathbf{R}$. Since the primary space and consequently the projector P are invariant under a change of the single-particle basis, this also holds true when $\mathbf{R}$-dependent orbitals like, e.g., Hartree-Fock orbitals are chosen, as long as they form a complete basis of the single-particle space. Consequently a formulation employing the projection operators P and $Q=1-P$ remains independent of the choice of the single-particle basis and thus an $\mathbf{R}$ dependence of the orbitals does not matter.

We already discussed in Sec. III B that we want to adopt the Born-Oppenheimer approximation for the electronic ground state $|\Psi_0^N\rangle$. In particular, we assume the $\mathbf{R}$ dependence of the electronic ground state $|\Psi_0^N\rangle$ to be weak. As a consequence, the projection operator P commutes with the nuclear kinetic energy T_n and therefore also with H_n:

$$[P,T_n]=[P,H_n]=0. \qquad (72)$$

We want to stress once more that we assume the Born-Oppenheimer approximation only for the nuclear motion in the electronic ground state of the N-electron molecule, which is physically reasonable for many molecules. However, this neither implies adiabaticity for the scattering electron nor for excited states of the scattering complex. By way of contrast, the nonadiabatic coupling of the projectile motion to the nuclear motion, which can be very important for slow projectiles, is explicitly accounted for in our formalism.

Defining the operator $Q=1-P$ as a projector onto the secondary space (1 is here the identity operator in Y space [45]), we can easily partition Eq. (70) in order to obtain an effective equation in the primary space. We take the following steps.

Inserting the identity $1=P+Q$ into Eq. (70) yields

$$\breve{H}(P+Q)\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}=(E-H_n+E_{00})\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}. \qquad (73)$$

Acting on this equation with Q from the left and using $[Q,H_n]=0$, which follows from $[P,H_n]=0$, yields an equation for the secondary-space component of the total wave function $Q(|\Psi_{\text{tot}}(\mathbf{R})\rangle,0)^t$:

$$\breve{H}_{QP}P\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}=(E-H_n+E_{00}-\breve{H}_{QQ})Q\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}. \qquad (74)$$

Here we introduced the notation $\breve{H}_{QP}$ for the operator product $Q\breve{H}P$, etc. Using Eq. (74) to replace the secondary-space component from the P projection of Eq. (73) leads to the desired equation for the primary-space component of the wave function:

$$\left[\breve{H}_{PP}+H_n-E_{00}-\breve{H}_{PQ}\frac{1}{E-H_n+E_{00}-\breve{H}_{QQ}}\breve{H}_{QP}\right]$$
$$\times P\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}=EP\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}. \qquad (75)$$

This is the resulting form of the time-independent Schrödinger equation projected to the primary space. The projected component fulfills a pseudoeigenvalue equation with an energy-dependent operator on the left-hand side. This operator acts on the nuclear coordinates $\mathbf{R}$ and on the electronic coordinates, but only within the primary space, which is isomorphous to the one-particle space (as was discussed in Sec. III A).

In the following we will make contact to our previous formulation and identify the self-energy of the dynamical Green's function as the optical potential. The primary-space component of the wave function is given by

$$P\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}=\sum_q |Y_q\rangle\left[\langle Y_q|\begin{pmatrix}|\Psi_{\text{tot}}(\mathbf{R})\rangle\\0\end{pmatrix}\right]=\sum_q |Y_q\rangle f_q(\mathbf{R}), \qquad (76)$$

where $f_q(\mathbf{R})=\langle\Psi_0^N|a_q|\Psi_{\text{tot}}(\mathbf{R})\rangle$ is the effective wave function of Eq. (61) in the orbital representation. Taking the inner product of Eq. (75) with $\langle Y_p|$ from the left yields

$$\sum_q \left(\langle Y_p|\breve{H}|Y_q\rangle+(H_n-E_{00})\delta_{pq}\right.$$
$$\left.-\langle Y_p|\breve{H}Q\frac{1}{E-H_n+E_{00}-\breve{H}_{QQ}}Q\breve{H}|Y_q\rangle\right)f_q(\mathbf{R})$$
$$=Ef_p(\mathbf{R}). \qquad (77)$$

The first term on the left can be identified as the primary block $\underline{\underline{H}}_{aa}$ of Eq. (28), which splits into the zeroth-order energy matrix $\underline{\underline{\varepsilon}}$ and the static (i.e., energy-independent) part of the self-energy $\underline{\underline{\mathcal{A}}}(\infty)$ according to Eq. (43). Also the energy-dependent part of $\underline{\underline{\mathcal{A}}}(\omega)$ can be identified in Eq. (77) when the representation

$$Q=\sum_J{}' |Q_J\rangle\langle Q_J| \qquad (78)$$

is chosen for the projector to the secondary space. The sum Σ' runs over the basis states $|Q_J\rangle$ of the secondary space only [cf. Eqs. (26) and (27)]. We obtain

$$\sum_q [\varepsilon_{pq}+(H_n-E_{00})\delta_{pq}+\mathcal{A}_{pq}(\omega)]f_q(\mathbf{R})=Ef_p(\mathbf{R}). \qquad (79)$$

The effective Schrödinger equation in the form of Eq. (64) is obtained when using the coordinate representation instead of the orbital representation for the scattering electron and realizing that the matrix $\underline{\underline{\varepsilon}}$ is the orbital representation of the operator $H_{e,0}$ of Eq. (32) in the one-electron space. As discussed earlier in this subsection, the projection operators P and Q are completely independent of the choice of the single-particle basis and thus Eq. (79) holds in the momentum, in the coordinate space, and in arbitrary orbital representations. We are also not restricted to a particular choice of the zeroth-order electronic Hamiltonian $H_{e,0}$, represented by the matrix $\underline{\underline{\varepsilon}}$ in Eq. (79). Any single-particle operator, which may or may not depend on $\mathbf{R}$, is possible. A convenient choice for the electron-molecule scattering problem is cer-

tainly to choose the Hartree-Fock operator for $H_{e,0}$ because this simplifies the calculation of the self-energy $\mathcal{A}(\omega)$. In this case, $H_{e,0}$ contains the electronic kinetic energy as well as the static-exchange potential.

So far, we have proven that the projection $f(\boldsymbol{r},\boldsymbol{R})$ of Eq. (61) of the physical scattering wave function fulfills the effective Schrödinger equation (64). There are also unphysical solutions of this equation due to the introduction of the second component in Eq. (70). The unphysical component lives in the Hilbert space of $N-1$ electrons, coupled to the same nuclear degrees of freedom as the physical component. Since the Hamiltonian for the second component from Eq. (70) is given by

$$V_0(\boldsymbol{R})-H_e+H_n-E_{00}=-[H_e-T_n-2V_0(\boldsymbol{R})+E_{00}], \quad (80)$$

the nuclear dynamics is not treated in the correct way to describe an ionized molecule because H_e and T_n have opposite sign. If we want to apply the formalism of the dynamical optical potential to describe the dynamics of ionized molecules, the definition of the Hamiltonian has to be changed accordingly.

Coming back to the description of the electron-scattering problem we want to consider the question of how to identify unphysical solutions and whether the unphysical component can interfere with the physical solutions. The answer to these questions is easily given when the scattering boundary conditions are obeyed correctly: Since the electronic ground state of the scattering target $|\Psi_0^N\rangle$ represents a bound state, any overlap $\langle\Psi|\psi(\boldsymbol{r})|\Psi_0^N\rangle$ is a square-integrable function of $\boldsymbol{r}$ vanishing asymptotically for $|\boldsymbol{r}|\rightarrow\infty$. Consequently, the same holds true for the effective wave function $f^{\text{unphys}}(\boldsymbol{r},\boldsymbol{R})$ belonging to an unphysical solution of Eq. (70),

$$f^{\text{unphys}}(\boldsymbol{r},\boldsymbol{R})=\left[\langle Y(\boldsymbol{r})|\binom{0}{\langle\Psi_{\text{unphys}}^{N-1}(\boldsymbol{R})|}\right]$$

$$=\langle\Psi_{\text{unphys}}^{N-1}(\boldsymbol{R})|\psi(\boldsymbol{r})|\Psi_0^N\rangle, \quad (81)$$

as a function of $\boldsymbol{r}$. As long as one solves the effective Schrödinger equation (64) or the corresponding Lippmann-Schwinger equation imposing scattering boundary conditions on the effective wave function $f(\boldsymbol{r},\boldsymbol{R})$, one obtains a physical solution. Even a contamination of the physical solution with a short-range unphysical solution will do no harm because for the calculation of the S-matrix elements only the asymptotic behavior of the effective wave function enters.

Let us briefly examine the only approximation made in the derivation of Eq. (75). Without the approximation (72), which allowed the commutation of the nuclear kinetic energy T_n with the projection operators P and Q, additional terms proportional to PH_nQ and QH_nP appear in the projected Schrödinger equation. These terms describe virtual excitations from the primary to the secondary space, which mean an electronic excitation in the target molecule, mediated by the nuclear kinetic-energy operator. These terms compete with excitations by the electronic Hamiltonian PH_eQ and QH_eP against which they can usually be neglected. The only exemption may be given in cases where the Born-Oppenheimer approximation for the electronic ground state fails and the potential surfaces of the electronic ground and excited states of the target molecule come close to each

other. In these rare cases, the vibronic interactions have to be accounted for and a diabatic representation for the ground state may be adequate. The dynamical optical potential then has to be augmented by terms that describe the corresponding vibronic transitions.

D. Approximative scattering equations

In this subsection we want to discuss different approximations to the exact scattering equations and the physical models these approximations imply. In the first two points we will consider possibilities to regain well-known approximate descriptions of electron-molecule scattering by either neglecting the energy-dependent optical potential or by freezing the nuclear degrees of freedom in the exact equation (67). In the last two points we will concentrate on the dynamical optical potential itself. Apart from discussing the role of the nuclear dynamics within the optical potential we will show how to compute ab initio dynamical optical potentials.

1. Static approximations to the optical potential

First of all we want to consider the simplest of all approximations to the optical potential, which results by neglecting the optical potential $\mathcal{A}(\omega)$ altogether. Formally this approximation is equivalent to neglecting the interaction part $H_{e,1}$ in the electronic Hamiltonian H_e of Eq. (31). This equivalence follows easily from Eq. (44), which connects the dynamical self-energy $\mathcal{A}(\omega)$ to the usual self-energy $\Sigma(\omega)$, which is by definition at least of first order in $H_{e,1}$ [12]. In other words we can say that, neglecting the dynamical self-energy $\mathcal{A}(\omega)$, the effective Schrödinger equation (64) is still exact for physical systems where the scattering electron is not correlated with other electrons in the system and thus is well described by $H_{e,0}$. The one-particle operator $H_{e,0}$ may still contain mean fields or forces exerted by the atomic nuclei or external fields, of course.

The level of approximation gained with the resulting static (i.e., energy-independent) Layzer operator $\mathcal{L}^{st}=H_{e,0}+H_n-E_{00}$ depends on the choice of the zeroth-order electronic Hamiltonian $H_{e,0}$.

(1) Choosing $H_{e,0}$ to describe the electronic kinetic energy yields a Layzer operator $\mathcal{L}^{st}$ that describes the separable motion of a free electron and a vibrating or rotating target molecule in its electronic ground state.

(2) Choosing instead $H_{e,0}$ to describe the $\boldsymbol{R}$-dependent Hartree-Fock operator yields a static Layzer operator that describes the motion of the scattering electron under the influence of the static and the exchange interactions with the Hartree-Fock charge cloud of the target molecule coupled to the nuclear motion in the usual electronic-ground-state potential $V_0(\boldsymbol{R})$ augmented by the Coulomb attraction between the nuclei and the electronic projectile. This approximation gives a consistent treatment of the electron-molecule scattering problem in the strict single-particle picture. Projectile and nuclear motion are fully coupled but the very nature of this static approximation excludes polarization effects as well as the possibility of electronic excitation of the target caused by the impact of the scattering projectile. Another defect of this Hartree-Fock based static-exchange approximation is that the static charge cloud of the target molecule is

only described in an approximate (uncorrelated) manner through the Hartree-Fock wave function.

Another straightforward possibility for an energy-independent approximation to the dynamical optical potential is to include the high-energy limit of the self-energy $\mathcal{A}(\infty)$, which is also called the static self-energy. The static part of the dynamical self-energy $\mathcal{A}(\infty)$ is identical to the purely electronic static self-energy $\Sigma(\infty)$, as can be seen from Eqs. (35) and (43) [see also Eq. (44)]. As shown in Ref. [56], this nonlocal operator can be interpreted to improve the static-exchange interaction beyond the Hartree-Fock description of the target wave function including target correlation. The present approximation to the Layzer operator $\mathcal{L}^{\text{CSE}} = H_{e,0} + H_n + \mathcal{A}(\infty) - E_{00}$ is independent of the choice of the zeroth-order electronic Hamiltonian $H_{e,0}$ in Eq. (31) because the static self-energy takes account of the interaction term $H_{e,1}$. The Layzer operator $\mathcal{L}^{\text{CSE}}$ corresponds to a scattering potential that originates from a correlated but static charge distribution of the target molecule, which is also known as the correlated static-exchange (CSE) potential.

Approximations to the energy-dependent part of the dynamical optical potential in the context of the fully coupled scattering problem will be discussed in Secs. IV D 3 and IV D 4. In the following paragraph we will consider the simplified case where the nuclear dynamics is neglected altogether.

2. Fixed-nuclei scattering

Let us recall that the full Layzer operator $\mathcal{L}$ may be expressed with the help of Eq. (44) by

$$\mathcal{L}(E) = H_{e,0} + T_n + V_0(\boldsymbol{R}) + \Sigma[E - T_n - V_0(\boldsymbol{R}) + E_{00}] - E_{00}. \tag{82}$$

In the limit of infinitely heavy nuclei, the nuclear kinetic energy T_n can be neglected. We call this limit the *fixed-nuclei* (FN) limit because the Layzer operator

$$\mathcal{L}^{\text{FN}}(E) = H_{e,0} + \Sigma[E - V_0(\boldsymbol{R}) + E_{00}] + V_0(\boldsymbol{R}) - E_{00} \tag{83}$$

and the corresponding scattering wave function $f(\boldsymbol{r},\boldsymbol{R})$ of Eq. (64) now depends only parametrically on the nuclear coordinates $\boldsymbol{R}$. The operator $\mathcal{L}^{\text{FN}}(E)$ is exactly the Layzer operator used in the literature for electron scattering from atoms or rigid molecules [4,49,5] apart from the $\boldsymbol{R}$-dependent energy shift $V_0(\boldsymbol{R}) - E_{00}$. This energy shift resets the zero point of the energy scale from E_{00} to $V_0(\boldsymbol{R})$.

In the present case of fixed-nuclei scattering, the optical potential is given by the purely electronic self-energy $\Sigma(\omega)$. As mentioned earlier, the static part $\Sigma(\infty)$ improves the static-exchange potential with respect to the correlation of the target's electronic-ground-state wave function. The energy-dependent part $M(\omega) = \Sigma(\omega) - \Sigma(\infty)$ is, according to Eq. (35), given by

$$\underline{M}(\omega) = \underline{\breve{H}}_{ab} \frac{1}{\omega \underline{1} - \underline{\breve{H}}_{bb}} \underline{\breve{H}}_{ba}. \tag{84}$$

For convenience, we again resort to the matrix notation for electronic coordinates used already in the preceding sections. Of course, the matrices can also be expressed in the coordi-

nate representation. $M(\omega)$ accounts for the so-called dynamic correlation including the polarization of the target by the incident projectile electron [57]. The energy dependence of $M(\omega)$ has been studied in the literature [58] and the consequences of the energy dependence of optical potentials for scattering systems have been discussed [2]. Here, we briefly want to remark the following.

$M(\omega)$ introduces poles and branch cuts in the optical potential, which can be found by diagonalizing the denominator of Eq. (84). The matrix $\underline{\breve{H}}_{bb}$ in the denominator is already diagonal in zeroth order, e.g., in the Hartree-Fock approximation. The diagonal elements correspond to electronic excitations of the $(N+1)$- and $(N-1)$-electron systems and can be classified by configurations of $2p$-h, $3p$-$2h$, etc. character as well as configurations of p-$2h$, $2p$-$3h$ type, and so on. Explicit matrix representations for $\underline{\breve{H}}_{ab}$, $\underline{\breve{H}}_{ba}$, and $\underline{\breve{H}}_{bb}$ can be found in Ref. [42].

For the calculation of $\Sigma(\omega)$, standard approximation schemes are available. The so-called algebraic diagrammatic construction (ADC) scheme [14], for example, yields a perturbation-theory-based hierarchy of approximations for $\Sigma(\omega)$ that preserve the analytic structure of this function of ω, in contrast to ordinary perturbation theory, which does not. The ADC approximation to $\Sigma(\omega)$ has the structure of Eq. (35) but the matrices $\underline{\breve{H}}_{ij}$ are constructed in the nth-order ADC scheme such that the perturbation expansion of the approximate $\Sigma^{\text{ADC}}(\omega)$ with respect to the electronic interaction $H_{e,1}$ of Eq. (31) coincides up to nth order with the usual Feynman-Dyson perturbation series of $\Sigma(\omega)$.

Since the poles and cuts relating to the ionized molecule $(N-1$ electrons$)$ appear at negative energies, they only have a weak influence on the energy dependence of the optical potential at the relevant scattering energies. The poles and cuts at positive energies, however, can be associated with excited states of the $(N+1)$-electron scattering system. Signatures of Feshbach resonances therefore can be found in the dynamic part of the optical potential although the exact resonance position and width, of course, have to be calculated from the full effective Hamiltonian. A branch cut will appear in the analytic structure of $\Sigma(\omega)$ above the first excitation energy of the target molecule because with sufficient energy for an electronic excitation, a new channel opens and inelastic scattering becomes possible. The branch cut of $\Sigma(\omega)$ has the consequence that the optical potential acquires an imaginary component and becomes non-Hermitian, thereby accounting for the loss of amplitude in the channel of electronically elastic scattering.

3. Nuclear dynamics in the optical potential: Expansion with respect to T_n

We are now going to discuss the influences of the nuclear motion on the dynamical optical potential $\mathcal{A}(E)$. The dynamical self-energy $\mathcal{A}(E)$ as given by Eq. (43) consists of an energy-independent (static) part $\mathcal{A}(\infty)$ and an energy-dependent part $\mathcal{M}(E) = \mathcal{A}(E) - \mathcal{A}(\infty)$, which vanishes for large energies E. The energy-dependent part $\mathcal{M}(E)$ includes all effects of dynamic correlation including polarization but is now modified with respect to the fixed-nuclei case considered in Sec. IV D 2. As follows from Eq. (43), the energy-dependent part reads in matrix notation

$$\underset{=}{\mathcal{M}}(E) = \underset{=}{\breve{H}}_{ab} \frac{1}{[E - T_n - V_0(\boldsymbol{R}) + E_{00}]\underset{=}{\mathbb{1}} - \underset{=}{\breve{H}}_{bb}} \underset{=}{\breve{H}}_{ba}. \quad (85)$$

As before, T_n denotes the nuclear kinetic energy, $V_0(\boldsymbol{R})$ the (electronic) ground-state potential, E is the scattering energy, and E_{00} the molecular ground-state energy. The matrices $\underset{=}{\breve{H}}_{ij}$ are the partial matrix representations of the two-component electronic excitation-energy operator $\underset{=}{\breve{H}}$, introduced in Sec. III A, and depend on the nuclear coordinates $\boldsymbol{R}$. In order to diagonalize the denominator to find the pole structure of $\underset{=}{\mathcal{M}}(E)$, not only eigenvectors of $\underset{=}{\breve{H}}_{bb}$ corresponding to electronic eigenstates in the secondary space are necessary but instead one also has to consider the additional degrees of freedom of nuclear motion. Since the energies usually associated to the nuclear dynamics are much smaller than typical energies of electronic excitations, we may assume that the coarse structure of the energy dependence does not differ much from the fixed-nuclei case discussed in Sec. IV D 2. However, the nuclear dynamics will introduce a fine structure and may become very important, either at energies where electronic excitation is possible or nearly possible, or in situations that are very sensitive to disturbance of the scattering potential, e.g., close to vibrationally inelastic thresholds.

As long as the scattering energies are safely away from Feshbach resonances or inelastic thresholds, the influences of nuclear dynamics on the optical potential itself may either be neglected or accounted for approximately by expansions of the denominator in Eq. (85). We will now proceed to discuss two convenient expansions for $\underset{=}{\mathcal{M}}(E)$.

Closest in spirit to the previously discussed fixed-nuclei approximation is the assumption that T_n represents a small perturbation, suggesting the following type of expansion:

$$\underset{=}{\mathcal{M}}(E) = \underset{=}{\breve{H}}_{ab} \frac{1}{[E - V_0(\boldsymbol{R}) + E_{00}]\underset{=}{\mathbb{1}} - \underset{=}{\breve{H}}_{bb}}$$
$$\times \sum_{\nu=0}^{\infty} \left(T_n \frac{1}{[E - V_0(\boldsymbol{R}) + E_{00}]\underset{=}{\mathbb{1}} - \underset{=}{\breve{H}}_{bb}} \right)^{\nu} \underset{=}{\breve{H}}_{ba}.$$
$$(86)$$

In the present context, we call the first term of this expansion ($\nu = 0$) the *adiabatic optical potential* (AOP):

$$\underset{=}{\mathcal{A}}^{\mathrm{AOP}}(E) = \underset{=}{\breve{H}}_{aa} - \underset{=}{\boldsymbol{\varepsilon}} + \underset{=}{\breve{H}}_{ab} \frac{1}{[E - V_0(\boldsymbol{R}) + E_{00}]\underset{=}{\mathbb{1}} - \underset{=}{\breve{H}}_{bb}} \underset{=}{\breve{H}}_{ba}$$
$$= \underset{=}{\Sigma}[E - V_0(\boldsymbol{R}) + E_{00}]. \quad (87)$$

Formally, the adiabatic optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$ coincides with the optical potential used in fixed-nuclei scattering in Sec. IV D 2. The difference is that the nuclear coordinates $\boldsymbol{R}$ are now dynamical variables. The adiabatic optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$ is a local operator on the nuclear coordinates $\boldsymbol{R}$ because V_0 and the matrices $\underset{=}{\breve{H}}_{ij}$ depend on $\boldsymbol{R}$ but there are no derivatives with respect to $\boldsymbol{R}$ in $\mathcal{A}^{\mathrm{AOP}}(E)$. Since $\mathcal{A}^{\mathrm{AOP}}(E)$ can be calculated, for each $\boldsymbol{R}$, from the purely electronic

self-energy $\Sigma(E)$, standard techniques for calculating the electronic self-energy like the ADC method mentioned in Sec. IV D 2 can be applied.

The Layzer operator corresponding to the presently discussed approximative treatment of the dynamical optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$ is given by

$$\mathcal{L}^{\mathrm{AOP}}(E) = H_{e,0} + H_n + \mathcal{A}^{\mathrm{AOP}}(E) - E_{00}. \quad (88)$$

Although the dynamical optical potential is treated here in an adiabatic approximation, the Layzer operator $\mathcal{L}^{\mathrm{AOP}}(E)$ describes the fully and nonadiabatically coupled motion of the projectile electron and the atomic nuclei with a simplified optical potential. In this approximation, the nuclear dynamics in the electronically excited states of the target is treated adiabatically. Even though this approximation may not be justified when describing experiments probing in detail the electronic excitation structure of the target, the situation is different for scattering at low but not too low energies. When electronic excitations are forbidden by energy conservation because the electron-impact energy is too low, the adiabatic approximation $\mathcal{A}^{\mathrm{AOP}}(E)$ may be very good. At low impact energies, electronic excitation then is still possible as a virtual process leading to polarization of the molecule but obeying the energy-time uncertainty relation. When the typical times for these virtual excitations are much smaller than the time scales of nuclear vibrations, which will usually be the case, then the fixed-nuclei approximation for the dynamical optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$ is adequate.

For very slow scattering electrons, on the other hand, it may also be necessary to improve the approximation $\mathcal{A}^{\mathrm{AOP}}(E)$, when the cross sections probe the details of the optical potential very sensitively. In the adiabatic optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$, the dynamical relaxation of the nuclear structure during the polarization of the electronic charge cloud induced by the incoming projectile is not treated properly. At very low projectile velocities where the trajectories are most sensitive on the coupling to the nuclear motion this may become an important defect of the theory. In this case the expansion of the dynamical optical potential discussed in the next subsection, which allows for an approximate treatment of the neglected effects, becomes most valuable.

4. Expansion of the dynamical optical potential with respect to $H_n - E_{00}$

The nuclear kinetic-energy operator T_n introduces derivatives with respect to the nuclear coordinates $\boldsymbol{R}$ in the terms of the expansion (86) for $\nu \geq 1$. In general, these terms will be difficult to evaluate because the approximate and also the exact matrices $\underset{=}{\breve{H}}_{ij}$ may depend strongly on the nuclear coordinates $\boldsymbol{R}$ due to the electron-nucleon Coulomb repulsion contained in $\breve{H}$. Another expansion that is better suited for higher-order approximations is obtained when taking $T_n + V_0(\boldsymbol{R}) - E_{00} = H_n - E_{00}$ as the "small" perturbation. The assumption that $H_n - E_{00}$ may be regarded small in the denominator of Eq. (85) is justified when the energies associated to nuclear excitations appearing during the scattering process and possibly during (virtual) electronic excitations are small compared to the electronic excitation energies of the target. The corresponding expansion of the energy-dependent part of the dynamical self-energy reads

$$\underline{\underline{\mathcal{M}}}(E)=\underline{\underline{\breve{H}}}_{ab}\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}}\sum_{\nu=0}^{\infty}\left[(H_n-E_{00})\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}}\right]^{\nu}\underline{\underline{\breve{H}}}_{ba}. \tag{89}$$

The first term $\underline{\underline{\mathcal{M}}}^0(E)$ of this expansion ($\nu=0$) can be identified as the energy-dependent (dynamic) part of the purely electronic self-energy (84) and will be called the *zero-point optical potential* because it reflects the optical potential of ground-state nuclear motion:

$$\underline{\underline{\mathcal{M}}}^0(E)=\underline{\underline{\breve{H}}}_{ab}\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}}\underline{\underline{\breve{H}}}_{ba}=\underline{\underline{M}}(E).$$

The zero-point optical potential is a local operator with respect to the nuclear coordinates $\boldsymbol{R}$ like the adiabatic optical potential $\underline{\underline{\mathcal{M}}}^{\mathrm{AOP}}(E)$, which was discussed above.

The higher-order terms in the expansion for $\nu\geqslant1$, however, are differential operators in the nuclear coordinates. They can be transformed into nonlocal integral operators $\underline{\underline{\mathcal{M}}}^{\nu}(E)f(\boldsymbol{R})=\int d\boldsymbol{R}'\,\underline{\underline{\mathcal{M}}}^{\nu}(E,\boldsymbol{R},\boldsymbol{R}')f(\boldsymbol{R}')$ by inserting the resolution of the identity with respect to nuclear motion $\Sigma_k|\phi_k\rangle\langle\phi_k|$. In the coordinate representation for the nuclear degrees of freedom $\boldsymbol{R}$, the integral kernel belonging to the second term of the expansion (89) reads

$$\underline{\underline{\mathcal{M}}}^1(E,\boldsymbol{R},\boldsymbol{R}')=\sum_k\underline{\underline{\breve{H}}}_{ab}(\boldsymbol{R})\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}(\boldsymbol{R})}\phi_k(\boldsymbol{R})$$
$$\times[E_{0k}-E_{00}]\phi_k^*(\boldsymbol{R}')$$
$$\times\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}(\boldsymbol{R}')}\underline{\underline{\breve{H}}}_{ba}(\boldsymbol{R}'), \tag{90}$$

where we explicitly indicated the nuclear-coordinate dependence of the matrices $\underline{\underline{\breve{H}}}_{ij}$. The numerical realization of this approximation is not very difficult because the nuclear eigenvalues E_{0k} and functions $\phi_k(\boldsymbol{R})$ can be calculated easily from the ground-state potential $V_0(\boldsymbol{R})$ and approximate matrices $\underline{\underline{\breve{H}}}_{ij}$ are available, e.g., by the ADC approximation as described above in Sec. IV D 2.

Equation (90) is remarkable because it allows us to estimate the importance of the higher-order terms in the expansion (89). If the nuclear dynamics of the target molecule, in spite of virtual excitations by the scattering electron, can be approximated well by the zero-point vibration of the isolated molecule (in its electronic ground state) then all terms with $k\neq0$ in Eq. (90) can be neglected. Since, however, the energy difference $[E_{0k}-E_{00}]$ vanishes for $k=0$, the term $\underline{\underline{\mathcal{M}}}^1(E)$ and the higher-order terms in Eq. (89) vanish. In this approximation only the zeroth term $\underline{\underline{\mathcal{M}}}^0(E)$ contributes in the expansion of the dynamical optical potential. In other words, $\underline{\underline{\mathcal{M}}}(E)$ is a local operator in the nuclear coordinates if the nuclear-coordinate dependence of the effective scattering wave function $f(\boldsymbol{r},\boldsymbol{R})$ is given by the nuclear eigenfunction $\phi_0(\boldsymbol{R})$ and the $\boldsymbol{R}$ dependence of the matrices $\underline{\underline{\breve{H}}}_{bb}$ and $\underline{\underline{\breve{H}}}_{ba}$ can be neglected. This will not always be the case. However, it can also be tested during a calculation for which values of k the integral

$$\int d\boldsymbol{R}\phi_k^*(\boldsymbol{R})\frac{1}{E\underline{\underline{1}}-\underline{\underline{\breve{H}}}_{bb}(\boldsymbol{R})}\underline{\underline{\breve{H}}}_{ba}(\boldsymbol{R})f(\boldsymbol{R}) \tag{91}$$

gives the largest contribution. The approximation $\underline{\underline{\mathcal{M}}}^0(E)$ can then be improved by expanding around $H_n-\widetilde{E}$, where $\widetilde{E}$ is a suitably chosen mean vibrational (rotational) energy, instead of H_n-E_{00}, yielding the zeroth approximation

$$\underline{\underline{\mathcal{M}}}^{\widetilde{0}}=\underline{\underline{\Sigma}}(E+E_{00}-\widetilde{E})-\underline{\underline{\Sigma}}(\infty) \tag{92}$$

and the corresponding higher approximations as in Eq. (89).

The difference between the adiabatic optical potential $\mathcal{A}^{\mathrm{AOP}}(E)$ and the zero-point optical potential $\mathcal{A}^0(E)$ or the improved approximation $\mathcal{A}^{\widetilde{0}}(E)$ lies in the energy reference of the denominator of the optical potential. We expect $\mathcal{A}^0(E)$ or $\mathcal{A}^{\widetilde{0}}(E)$ to be suitable approximations for $\mathcal{A}(E)$ when the nuclear motion is more or less confined to the immediate surroundings of the equilibrium configuration $\boldsymbol{R}_{eq}$ of the molecule. In particular, for processes that travel between different levels on the potential energy surface $V_0(\boldsymbol{R})$ corresponding to a considerable transfer of energy between the projectile and target like it happens in associative detachment or dissociative attachment, we expect the adiabatic approximation $\mathcal{A}^{\mathrm{AOP}}(E)$ to be the better-suited approximation. However, we want to stress once again that the treatment of the nuclear dynamics within the optical potential is certainly less essential than the direct coupling between projectile and nuclear motion in the effective Schrödinger equation (64), as long as the scattering energy remains well below the threshold for electronic excitation of the molecular target. The expansion (89) presents a systematic possibility to improve upon the adiabatic or the zero-point approximation that is applicable if the scattering process has too little energy to access the electronically excited states of the target. The first-order term $\underline{\underline{\mathcal{M}}}^1$ of Eq. (90) and the corresponding higher approximations provide access to a systematic improvement of the discussed approximations for *ab initio* methods of quantum chemistry that may prove necessary to describe the dynamical couplings correctly for very-low-energy scattering processes that are particularly sensitive to the correct description of the optical potential. If the scattering energy is above or close to the threshold for electronic excitation of the target molecule, the effective Schrödinger equation (64) still remains valid but other approximations to the dynamical optical potential have to be used.

V. CONCLUSIONS

In this paper we have derived a rigorous optical potential for the coupled motion of the projectile electron and the atomic nuclei in electron-molecule scattering. The dynamical optical potential should be particularly valuable for studying the nonadiabatic coupling of projectile and nuclear motion close to inelastic thresholds where the projectile velocity is comparable to the typical velocities of nuclear motion. Our work extends the well-known many-body formalism of optical potentials beyond the fixed-nuclei approximation. On the other hand, the rigorous derivation and the explicit expressions given for the dynamical optical potential provide a justification and prospective for enhancement of model polar-

ization potentials used commonly in close-coupling and *R*-matrix calculations.

The dynamical optical potential can describe all kinds of electronically elastic scattering processes such as elastic scattering, vibrational or rotational excitation (deexcitation), dissociative attachment, and associative detachment. Also when electronic excitations are energetically accessible, the dynamical optical potential may be used to calculate the (electronically) elastic partial cross sections as well as resonance positions and widths.

One central result of the present work is that for scattering energies far enough away from electronic excitations of the target, the dynamical optical potential is given in a first approximation by the static-exchange potential augmented by the fixed-nuclei self-energy $\Sigma(\omega)$ of the purely electronic Green's function. This approximation, which yields a local operator with respect to the nuclear coordinates R, can be improved by a hierarchy of nonlocal terms. Due to the close relation to the usual self-energy $\Sigma(\omega)$, all terms can be calculated with standard *ab initio* methods using well-defined approximation schemes.

The dynamical optical potential provides a firm basis for theoretical studies of coupled projectile and nuclear motion in ultralow-energy electron-molecule scattering, which is becoming a vivid field of interest due to recent experimental advances (see, e.g., [59]). The effective scattering equations presented in this paper can be solved, e.g., by using close-coupling expansions or other time-independent techniques. We expect that particularly valuable insight into the mechanisms of the scattering process, however, can be gained by time-dependent wave-packet calculations. Solving these scattering equations certainly remains a numerically demanding task but becomes more and more feasible now with state of the art computing facilities and the advancement of numerical methods [60].

ACKNOWLEDGMENTS

[1] H. Feshbach, *Theoretical Nuclear Physics: Nuclear Reactions* (Wiley, New York, 1992).

[2] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958).

[3] H. Feshbach, Ann. Phys. (N.Y.) **19**, 287 (1962).

[4] J. S. Bell and E. J. Squires, Phys. Rev. Lett. **3**, 96 (1959).

[5] G. Y. Csanak, H. S. Taylor, and R. Yaris, Adv. At. Mol. Phys. **7**, 287 (1971).

[6] P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer, New York, 1980), p. 623ff.

[7] C. Mahaux and R. Sartor, Nucl. Phys. A **530**, 303 (1991).

[8] B. I. Schneider and L. A. Collins, J. Phys. B **15**, L335 (1982).

[9] B. I. Schneider and L. A. Collins, Phys. Rev. A **27**, 2847 (1983).

[10] B. H. Lengsfield III and T. N. Rescigno, Phys. Rev. A **44**, 2913 (1991).

[11] T. J. Gil, C. W. McCurdy, T. N. Rescigno, and B. H. Lengsfield III, Phys. Rev. A **47**, 255 (1993).

[12] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, 1st ed. (McGraw-Hill, New York, 1971).

[13] B. Schneider, H. S. Taylor, and R. Yaris, Phys. Rev. A **1**, 855 (1970).

[14] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28**, 1237 (1983).

[15] J. V. Ortiz, J. Chem. Phys. **89**, 6348 (1988).

[16] A. Klonover and U. Kaldor, Chem. Phys. Lett. **51**, 321 (1977).

[17] A. Klonover and U. Kaldor, J. Phys. B **11**, 1623 (1978).

[18] A. Klonover and U. Kaldor, J. Phys. B **12**, 323 (1979).

[19] M. Berman, O. Walter, and L. S. Cederbaum, Phys. Rev. Lett. **50**, 1979 (1983).

[20] H.-D. Meyer, Phys. Rev. A **40**, 5605 (1989).

[21] E. P. Wigner and L. Eisenbud, Phys. Rev. **26**, 29 (1947).

[22] C. J. Gillan, O. Nagy, P. G. Burke, L. A. Morgan, and C. J. Noble, J. Phys. B **20**, 4585 (1987).

[23] K. Pfingst, B. M. Nestmann, and S. D. Peyerimhoff, J. Phys. B **27**, 2283 (1994).

[24] R. R. Lucchese, K. Takatsuka, and V. McKoy, Phys. Rep. **131**, 147 (1986).

[25] W. H. Miller and B. M. D. D. Jansen op de Haar, J. Chem. Phys. **86**, 6213 (1987).

[26] C. W. McCurdy, T. N. Rescigno, and B. I. Schneider, Phys. Rev. A **36**, 2061 (1987).

[27] N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980).

[28] M. A. Morrison and W. Sun, in *Computational Methods for Electron-Molecule Collisions*, edited by W. M. Huo and F. A. Gianturco (Plenum Press, New York, 1995), Chap. 6, p. 131.

[29] D. M. Case, Phys. Rev. **104**, 838 (1956).

[30] A. Temkin and K. V. Vasavada, Phys. Rev. **160**, 109 (1967).

[31] M. A. Morrison, A. N. Feldt, and B. C. Saha, Phys. Rev. A **30**, 2811 (1984).

[32] J. K. O'Connell and N. F. Lane, Phys. Rev. A **27**, 1893 (1983).

[33] M. A. Morrison, B. C. Saha, and T. L. Gibson, Phys. Rev. A **36**, 3682 (1987).

[34] M. A. Morrison and W. K. Trail, Phys. Rev. A **48**, 2874 (1993).

[35] M. A. Morrison, W. Sun, W. A. Isaacs, and W. K. Trail, Phys. Rev. A **55**, 2786 (1997).

[36] L. S. Cederbaum and W. Domcke, J. Phys. B **14**, 4665 (1981).

[37] W. Domcke, Phys. Rep. **208**, 97 (1991).

[38] M. Čížek, J. Horáček, and W. Domcke, J. Phys. B **31**, 2571 (1998).

[39] O. H. Crawford, Mol. Phys. **40**, 585 (1971).

[40] So far authors have only treated the $J=0$ case, ignoring the problems of higher angular momenta. In principle, they can be treated in the PO formalism but parameters for the angular momentum couplings are difficult to calculate directly and difficult to model as well. See, e.g., W. Domcke and C. Mündel, J. Phys. B **18**, 4491 (1985); J. Horáček, M. Čížek, and W. Domcke, Theor. Chem. Acc.**100**, 31 (1998).

[41] L. S. Cederbaum, Few-Body Syst. **21**, 211 (1996).

[42] A. Tarantelli and L. S. Cederbaum, Phys. Rev. A **45**, 2790 (1992).

[43] F. Capuzzi and C. Mahaux, Ann. Phys. (N.Y.) **245**, 147 (1996).

[44] J. Brand and L. S. Cederbaum, Ann. Phys. (N.Y.) **252**, 276 (1996).

[45] The vectors $|Y_p\rangle$ may be understood as elements of a composite Hilbert space Y that is a direct sum of the $(N+1)$-particle space and the dual space of the $(N-1)$-particle space $\mathsf{Y} = \mathsf{H}^{(N+1)} \oplus \mathsf{H}^{(N-1)*}$ where N is the number of electrons of the target molecule. The primary space, which is spanned by the composite states $|Y_p\rangle$, is only a (small) subspace of Y. The secondary space is defined by the orthogonal complement of the primary space in Y.

[46] F. Mertins, J. Schirmer, and A. Tarantelli, Phys. Rev. A **53**, 2153 (1996).

[47] The present derivation of Dyson's equation can also be formulated without reference to a particular basis of the primary or secondary space with the help of projection operators analogous to the derivation of the optical potential in Sec. IV C (see Ref. [43]). The $\boldsymbol{R}$ dependence of the projection operators is well defined and derives only from the electronic ground state $|\Psi_0^N\rangle$.

[48] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **90**, 5578 (1989).

[49] A. J. Layzer, Phys. Rev. **129**, 897 (1963).

[50] J. Aguilar and J. M. Combes, Commun. Math. Phys. **22**, 269 (1971).

[51] W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).

[52] G. Jolicard and E. J. Austin, Chem. Phys. Lett. **121**, 106 (1985).

[53] U. V. Riss and H.-D. Meyer, J. Phys. B **26**, 4503 (1993).

[54] T. Sommerfeld, U. V. Riss, H.-D. Meyer, L. S. Cederbaum, B. Engels, and H. U. Suter, J. Phys. B **31**, 4107 (1998).

[55] V. A. Mandelshtam, T. R. Ravuri, and H. S. Taylor, J. Chem. Phys. **101**, 8792 (1994).

[56] H.-G. Weikert and L. S. Cederbaum, Few-Body Syst. **2**, 33 (1987).

[57] H.-D. Meyer, J. Phys. B **21**, 3777 (1988).

[58] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 205 (1977).

[59] A. Schramm, J. M. Weber, J. Kreil, D. Klar, M.-W. Ruf, and H. Hotop, Phys. Rev. Lett. **81**, 778 (1998).

[60] *Numerical Grid Methods and their Application to Schrödinger's Equation*, edited by C. Cerjan (Kluwer Academic Publishers, Dordrecht, 1993).