Localized second-order optical potential for electron scattering in terms of imaginary-frequency susceptibilities

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A local approximation to the second-order optical potential for elastic scattering of low-energy electrons from ground-state atoms is expressed in terms of the imaginary-frequency susceptibilities of the atom due to a point charge and to modified perturbing potentials. This provides a basis for the physically appealing concept of regarding the perturbation due to the projectile as having a position-dependent effective frequency associated with it. The result is extended to higher energies with the use of the concept of a local kinetic energy. With a semiclassical approximation the result reduces to a simple general form that should be useful for model potential studies of electron-atom and electron-molecule scattering. Alternatively, variational functionals for the susceptibilities can be used to calculate the approximate optical potential most rigorously without making effective-frequency, average-kinetic-energy, or semiclassical approximations. Intermediate levels of rigor are also possible.

I. INTRODUCTION

The optical model provides a convenient and powerful tool for the quantum-mechanical treatment of electron scattering by atoms and molecules.[1−3] In this model the multichannel scattering problem involving all the target electronic degrees of freedom is replaced by a potential scattering problem involving electron scattering by the optical potential. In the optical model we cannot calculate the state-to-state cross sections for all individual final states of the target but we can calculate the differential and integral cross sections for electronically elastic scattering and the total integral cross section for the sum of all inelastic and ionization processes. An expression for an exact optical potential may be calculated by formal manipulation of the multichannel scattering equations.[4] In general though, one cannot afford a converged solution of these equations. More useful expressions for the optical potential can be obtained from linear-response theory and many-body perturbation theory.[1,3,5−7] In the present article we suggest a simple treatment based on the dynamic susceptibilities[8−10] of linear-response theory. Nonadiabatic effects are included because of the nonzero frequencies of the dynamic susceptibilities. We explicitly consider low energies where there is no electronic inelasticity but the treatment could be extended above the inelastic threshold by requiring

the optical potential to satisfy a dispersion relation.[4,11] Thus the resulting optical potential may be considered to be an improvement over the adiabatic exchange approximation[12,13] (which is closely related to the polarized orbital[14,15] method), in which an adiabatic polarization potential is added to the static-exchange potential, and nonadiabatic effects are neglected.

In addition to their intuitive appeal, frequency-dependent susceptibilities have the computational advantage that they may be evaluated by variational techniques.[8,10,16] The standard definition of the second-order optical potential includes a summation over all the excited states of the target.[1,3] The sum over excited states is a severe restriction on the usefulness of some expressions of the optical potential and is especially important if one tries to extend localized optical potentials that are valid for large separations of the projectile and target to ones that are valid at smaller separations. The ability to calculate frequency-dependent susceptibilities variationally rather than by an infinite sum is an important motivation for the present approach.

Our treatment in this paper explicitly deals only with electron scattering by atoms. For the extension to molecules one could fold all degrees of freedom of the target into the optical potential; however, a more useful procedure may be to use the optical model for the electronic degrees of freedom but treat the vibrational and rotational degrees of free-

dom dynamically or in a sudden limit.[17-19] In this kind of treatment the optical potential is a function of molecular geometry as well as the electron coordinate with respect to the molecule, and it may be calculated, in a separate calculation from the scattering calculation, using methods already developed for static-exchange potentials and other effective potentials.[17-19] Although one can hope for more rigorous treatments of electron-atom scattering at low energy, calculations for electron scattering by polyatomic molecules at intermediate energy are very difficult. We will keep the latter as our ultimate goal, and we will introduce approximations consistent with a problem at this level of difficulty, i.e., the low-energy electron-atom problem is serving merely as a testing ground for a model designed to be applicable to more intractable problems.

All equations in this paper are in Hartree atomic units in which $\hbar = m_e = a_0 = 1$.

II. LOCAL APPROXIMATION TO THE OPTICAL POTENTIAL

We begin by considering the coupled-channels expansion for the scattering wave function

$$\Psi(\vec{r},\vec{x}) = r^{-1} \sum_n \psi_n(\vec{x}) f_n(\vec{r}) , \qquad (1)$$

where $\vec{r}$ is a vector from the center of mass of the target to the scattering electron and $\vec{x}$ is the collection of target coordinates; the target eigenfunctions are $\psi_n(\vec{x})$ and satisfy

$$(\hat{H}_{int} - \epsilon_n) \psi_n(\vec{x}) = 0 . \qquad (2)$$

Equation (1) does not explicitly include the exchange of target and incident electrons; we assume exchange effects can be added to the theory later. Decompose the total Hamiltonian as

$$\hat{H} = \hat{H}_{int} + \hat{T} + V(\vec{r},\vec{x}) , \qquad (3)$$

where $V(\vec{r},\vec{x})$ is the interaction potential, T represents the relative kinetic energy

$$\hat{T} = -\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{l}^2}{2r^2} , \qquad (4)$$

and $\hat{l}$ is the orbital angular momentum operator for the scattering electron. The standard coupled-channels equations for the relative-motion wave functions are then

$$(\hat{t} + V_{00} - E_{rel}) f_0(\vec{r}) + \sum_n' V_{0n}(\vec{r}) f_n(\vec{r}) = 0 \qquad (5)$$

for $f_0(\vec{r})$ with similar equations for $f_n(\vec{r})$ with $n \neq 0$. Primes on summations denote that the $n = 0$ term is omitted, the relative translational energy is defined by

$$E_{rel} = E - \epsilon_0 , \qquad (6)$$

the kinetic energy operator in the reduced Eq. (5) is given by

$$\hat{t} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{\hat{l}^2}{2r^2} , \qquad (7a)$$

$$= \hat{t}_r + \hat{t}_a , \qquad (7b)$$

and we have introduced the static potential $V_{00}(\vec{r})$ and transition potentials $V_{0n}(\vec{r})$ where

$$V_{mn}(\vec{r}) = \int d\vec{x} \, \psi_n^*(\vec{x}) V(\vec{r},\vec{x}) \psi_n(\vec{x}) , \qquad (8)$$

$$= \langle m | V | n \rangle . \qquad (9)$$

According to Feshbach's theory of the optical potential, Eq. (5) may be replaced by

$$(\hat{t} + \hat{V}^{opt} - E_{rel}) f_0(\vec{r}) = 0 , \qquad (10)$$

where $\hat{V}^{opt}$ is the optical potential operator given by[4]

$$\hat{V}^{opt} = V_{00}(\vec{r}) + \left\langle 0 \left| VQ \frac{1}{Q[E - \hat{H}_{int} - \hat{t} - V(\vec{r},\vec{x})]Q} QV \right| 0 \right\rangle , \qquad (11)$$

where

$$Q = \sum_n' |n\rangle\langle n| . \qquad (12)$$

The second-order optical potential is obtained by expanding (11) to second order in the interaction potential. This yields

$$\hat{V}^{opt} \cong V_{00}(\vec{r}) + \hat{V}^{(2)} , \qquad (13)$$

where[3]

$$\hat{V}^{(2)} = \left\langle 0 \left| VQ \frac{1}{Q(E - \hat{H}_{int} - \hat{t})Q} QV \right| 0 \right\rangle \qquad (14a)$$

$$= -\sum_n' V_{0n}(\vec{r}) \frac{1}{\Delta_n - E_{rel} + \hat{t}} V_{n0}(\vec{r}) \qquad (14b)$$

and

$$\Delta_n = \epsilon_n - \epsilon_0 . \qquad (15)$$

Then, following Drachman,[20] we expand $\hat{V}^{(2)}$ in powers of $(E_{\text{rel}} - \hat{t})$, which represents the deviation from the adiabatic limit.[1-3] We retain only terms up to order $(E_{\text{rel}} - \hat{t})^2$. This is a low-energy approximation, and it yields

$$\hat{V}^{(2)} = -\sum_n{}' \frac{V_{0n}(\vec{r})}{\Delta_n} \left[1 + \frac{(E_{\text{rel}} - \hat{t})}{\Delta_n} \right.$$

$$\left. + \frac{(E_{\text{rel}} - \hat{t})^2}{\Delta_n^2} \right] V_{n0}(\vec{r}) . \qquad (16)$$

To continue further we will make two additional approximations. First we make the centrifugal sudden approximation[21] which consists of replacing the angular momentum operator in $\hat{t}$ by its initial eigenvalue, i.e.,

$$\hat{t} \cong \hat{t}_r + \tau_0(r) , \qquad (17)$$

where

$$\tau_0(r) = \frac{l_0(l_0 + 1)}{2r^2} , \qquad (18)$$

and l_0 is the initial value of the orbital angular momentum quantum number of the scattering electron. Second we make the zero-order approximation that when $\hat{V}^{(2)}$ of (16) operates on $f_0(\vec{r})$ and yields f_0'', where primes denote derivatives with respect to r, we may replace this quantity using

$$f_0'' \cong -2[E_{\text{rel}} - \tau_0(r) - V_{00}(\vec{r})]f_0(\vec{r}) \underline{\qquad} \quad (19)$$

$$= -2t_r(\vec{r})f_0(\vec{r}) . \qquad (20)$$

This defines a local approximation $t_r(\vec{r})$ to the radial kinetic energy. It may be considered a zeroth iterate to the self-consistent solution of

$$-\tfrac{1}{2}f_0'' + [\tau_0(r) + V_{00}(\vec{r}) + V^{(2)}(\vec{r}) - E_{\text{rel}}]f_0(\vec{r}) = 0 \qquad (21)$$

which results when (17) and the local approximation $V^{(2)}(\vec{r})$ are substituted into Eqs. (10) and (13). Substituting (7), (13), and (16) into (10) and using the approximations (17) and (19) yields

$$[\hat{t}_r + \tau_0(r) + V_{00}(\vec{r}) + u_0(\vec{r}) - E_{\text{rel}}]f_0(\vec{r}) + u_1(\vec{r})f_0' = 0 , \qquad (22)$$

where

$$u_0(\vec{r}) = -\sum_n{}' \frac{V_{0n}(\vec{r})}{\Delta_n} \left[V_{n0}(\vec{r}) + \frac{1}{\Delta_n}[V_{n0}(\vec{r})V_{00}(\vec{r}) + \tfrac{1}{2}V_{n0}''] \right.$$

$$+ \frac{1}{\Delta_n^2}\{ V_{n0}(\vec{r}) | V_{00}(\vec{r}) |^2 + \tfrac{1}{2}V_{n0}(\vec{r})V_{00}'' + V_{n0}'(2V_{00}' + \tau_0') $$

$$\left. + V_{n0}''[V_{00}(\vec{r}) - 2t_r(\vec{r})] + \tfrac{1}{4}V_{n0}'''' \} \right] \qquad (23)$$

and

$$u_1(\vec{r}) = -\sum_n{}' \frac{V_{0n}(\vec{r})}{\Delta_n} \left[\frac{V_{n0}'}{\Delta_n} + \frac{1}{\Delta_n^2}[V_{n0}(\vec{r})V_{00}' + 2V_{n0}'V_{00}(\vec{r}) + V_{n0}'''] \right] . \qquad (24)$$

The prime appearing on functions denotes differentiation with respect to r; the r dependence of derivatives is not shown explicitly. We see that the l-dependent terms have not been completely removed by the centrifugal sudden approximation. To proceed further we consider the case $l_0 = 0$. For $l_0 = 0$ the incident electron is sensitive to the potential at all $\vec{r}$. Thus if we obtain a good approximation for $l_0 = 0$, we may try as a further approximation to apply it for other l_0, for which the scattering is less sensitive to the small-r effective potential.

Equation (22) is not self-adjoint. To transform it to that form we make the transformation applied in a similar context by Seaton and Steenman-Clark[22]:

$$f_0(\vec{r}) = \exp \left[\int^r u_1(r',\hat{r})dr' \right] F_0(\vec{r}) . \qquad (25)$$

Then we obtain

$$[\hat{t}_r + V_{00}(\vec{r}) + V^{(2)}(\vec{r}) - E_{rel}]F_0(\vec{r}) = 0 , \tag{26}$$

where

$$V^{(2)}(\vec{r}) = u_0(\vec{r}) - \tfrac{1}{2}[u'_1 - |u_1(\vec{r})|^2] . \tag{27}$$

Neglecting $|u_1(\vec{r})|^2$, which is fourth order in the interaction potential, then yields

$$V^{(2)}(\vec{r}) = -\sum_n{}' \frac{1}{\Delta_n} \left[|V_{n0}(\vec{r})|^2 + \frac{1}{\Delta_n}[|V_{n0}(\vec{r})|^2 V_{00}(\vec{r}) - \tfrac{1}{2}|V'_{n0}|^2] \right.$$

$$+ \frac{1}{\Delta_n^2}\{ |V_{n0}(\vec{r})V_{00}(\vec{r})|^2 + 2V_{0n}(\vec{r})V''_{n0}[V_{00}(\vec{r}) - E_{rel}]$$

$$\left. - |V'_{n0}|^2 V_{00}(\vec{r}) - \tfrac{1}{2}V_{0n}(\vec{r})V''_{n0}{}' - \tfrac{1}{4}V_{0n}(\vec{r})V''_{n0}{}'' \} \right] . \tag{28}$$

This is a local approximation to the optical potential.

Although we have not made any explicit large-r approximations, the expansion in deviations from the adiabatic limit, Eq. (16), is most rapidly convergent at large r. To obtain a more accurate approximation at small and medium r, we resum the series. The resummation will be guided by our goal of eventually obtaining an approximation involving frequency-dependent polarizabilities.

One recognizes the beginnings of several series in (28). Consider first the terms involving no derivatives of $V_{n0}(\vec{r})$, and their sum, which we will call $V_1^{(2)}(\vec{r})$. We have

$$V_1^{(2)}(\vec{r}) = -\sum_n{}' |V_{n0}(\vec{r})|^2 \left[\frac{1}{\Delta_n} + \frac{V_{00}(\vec{r})}{\Delta_n^2} + \frac{[V_{00}(\vec{r})]^2}{\Delta_n^3} + \cdots \right] . \tag{29}$$

This series comes from the terms that would remain if $(\Delta_n - E_{rel} + \hat{t})^{-1}$ commuted with $V_{n0}(\vec{r})$ in (14b). It can be summed to yield

$$V_1^{(2)}(\vec{r}) = -\sum_n{}' \frac{|V_{n0}(\vec{r})|^2}{\Delta_n - V_{00}(\vec{r})} . \tag{30}$$

The second apparent series in (28) is

$$-\sum_n{}' |V'_{n0}|^2 \left[-\frac{1}{2\Delta_n^2} - \frac{V_{00}(\vec{r})}{\Delta_n^3} - \cdots \right] \cong +\sum_n{}' \frac{|V'_{n0}|^2}{2[\Delta_n - V_{00}(\vec{r})]^2} . \tag{31}$$

The series involving $V_{0n}(\vec{r})V''_{n0}$ is harder to recognize. However, before the cancellation involved in Eq. (27), this was

$$-\sum_n{}' V_{0n}(\vec{r})V''_{n0} \left[\frac{1}{2\Delta_n^2} + \frac{2[V_{00}(\vec{r}) - E_{rel}]}{\Delta_n^3} + \cdots - \frac{1}{2\Delta_n^2} \right]$$

$$\cong -\sum_n{}' \frac{V_{0n}(\vec{r})V''_{n0}}{2} \left[\frac{1}{\{\Delta_n + 2[E_{rel} - V_{00}(\vec{r})]\}^2} - \frac{1}{\Delta_n^2} \right] . \tag{32}$$

With these resummations we get

$$V^{(2)}(\vec{r}) \cong -\sum_n{}' \left[\frac{|V_{n0}(\vec{r})|^2}{\Delta_n - V_{00}(\vec{r})} - \frac{(V'_{n0})^2}{2[\Delta_n - V_{00}(\vec{r})]^2} + \frac{1}{2}\frac{V_{0n}(\vec{r})V''_{n0}}{\{\Delta_n + 2[E_{rel} - V_{00}(\vec{r})]\}^2} \right.$$

$$\left. - \frac{V_{0n}(\vec{r})V''_{n0}}{2\Delta_n^2} - \frac{V'_{0n}(\vec{r})V''_{n0}{}'}{2\Delta_n^2} - \frac{V_{0n}(\vec{r})V''_{n0}{}''}{4\Delta_n^3} \right] . \tag{33}$$

Although the resummation would be expected to improve the convergence at smaller r, the result is still a low-energy approximation. In particular, most of the terms do not go to zero in the limit of large E_{rel}. This is unphysical since the first Born approximation becomes valid at high E_{rel}, and this indicates that $V^{opt}(\vec{r})$ should tend to $V_{00}(\vec{r})$ is this limit. Thus further considerations or a different expansion as a starting point will be required to get a local approximation that has the correct high-energy limit. The high-energy case will be discussed again in Sec. V.

The fact that some of the nonadiabatic contributions are independent of incident energy at low energy is well known and has been discussed previously.[23-25] The physical basis for this effect is that a low-energy incident electron is speeded up so much upon approach to the nucleus that its incident speed has little effect on its local kinetic energy once it penetrates the screening electronic charge cloud. Thus the leading nonadiabatic effect at low energy is independent of incident energy. This result is obtained, for example, by the extended polarization model[23] where the leading low-energy nonadiabatic effect is contained in the energy-independent distortion potential.

Notice also that the present method yields a real valued $V^{(2)}(\vec{r})$. The imaginary part of the optical potential accounts for absorption of flux from the initial channel. An absorption potential could be estimated from the present approximation to the real part of the optical potential by using a dispersion equation.[11]

It is interesting to examine the large-r, low-energy expansion of the approximate optical potential of Eq. (33). For concreteness we consider a hydrogen atom as the target and call its electronic coordinate $\vec{r}_1$. Then

$$V(\vec{r},\vec{r}_1) \underset{r \to \infty}{\sim} -\frac{r_1}{r^2}P_1(\hat{r}_1 \cdot \hat{r}) - \frac{r_1^2}{r^3}P_2(\hat{r}_1 \cdot \hat{r}) , \quad (34)$$

$$V_{n0}(\vec{r}) \underset{r \to \infty}{\sim} -\frac{\mu_{n0}}{r^2} - \frac{\theta_{n0}}{r^3} , \quad (35)$$

$$V_{n0}' \underset{r \to \infty}{\sim} \frac{2\mu_{n0}}{r^3} , \quad (36)$$

and

$$V_{n0}'' \underset{r \to \infty}{\sim} -\frac{6\mu_{n0}}{r^4} , \quad (37)$$

where

$$\mu_{n0} = \langle n \mid r_1 P_1(\hat{r}_1 \cdot \hat{r}) \mid 0 \rangle \quad (38)$$

and

$$\theta_{n0} = \langle n \mid r_1^2 P_2(\hat{r}_1 \cdot \hat{r}) \mid 0 \rangle . \quad (39)$$

Substituting these expansions into (33) and noting that $V_{00}(\vec{r})$ decreases exponentially at large r, we obtain

$$V^{(2)}(\vec{r}) \underset{r \to \infty}{\sim} -\frac{\alpha_d}{2r^4} - \frac{\alpha_q}{2r^6} + \frac{2\beta}{r^6} + \frac{24\gamma E_{rel}}{r^6} + \cdots , \quad (40)$$

where we have used the standard definitions[20]

$$\alpha_d = 2\sum_n' \mu_{n0}^2/\Delta_n , \quad (41)$$

$$\alpha_q = 2\sum_n' \frac{\theta_{n0}^2}{\Delta_n} , \quad (42)$$

$$\beta = \sum_n' \frac{\mu_{n0}^2}{\Delta_n^2} , \quad (43)$$

and

$$\gamma = \frac{1}{2}\sum_n' \frac{\mu_{n0}^2}{\Delta_n^3} . \quad (44)$$

This may be compared to Drachman's result[20]

$$V^{(2)}(r) \sim -\frac{\alpha_d}{2r^4} - \frac{\alpha_q}{2r^6} + \frac{3\beta}{r^6} + \frac{24\gamma E_{rel}}{r^6} + \cdots . \quad (45)$$

The difference is in the coefficient for the β term, which has been derived by many workers.[23,24] Our coefficient is too small by a factor of $\frac{2}{3}$; this is a result of our use of Steenman-Clark and Seaton's method for treating the non-Hermitian term. Except for this difference, we see the present expression is an approximate generalization to all r of the more rigorous large-r expansion obtained by previous workers.[20,22,23,24]

Notice that (33) and (40) yield a spherically symmetric effective potential for S-state atoms but a nonspherical result for molecules.

III. LOCAL OPTICAL POTENTIAL IN TERMS OF FREQUENCY-DEPENDENT SUSCEPTIBILITIES

For the calculation of adiabatic interaction energies between atomic and molecular systems there is a computational advantage in writing the interaction energy as an integral over frequency-dependent polarizabilities.[16] For electron scattering, writing the optical potential in terms of

frequency-dependent susceptibilities should have two advantages. First there is the computational advantage that frequency-dependent susceptibilities can be calculated by a variational formalism. Secondly the introduction of the frequency-dependent-susceptibility language will provide insight into the physical nature of nonadiabatic effects.

The first term in the bracket in Eq. (16) corresponds to the zero-local-kinetic-energy limit for the scattering electron. Because the scattering electron is moving at a finite speed, the target response is more complicated than in the adiabatic limit. In principle, one could decompose the time-dependent interaction of the target with the scattering electron into its Fourier components and represent the interaction as an integral over the frequency-dependent susceptibilities of the target. The frequency-dependent susceptibility has poles at the target excitation frequencies and a branch cut for frequencies above that corresponding to the ionization potential.[26] In a theory that introduces approximations, it is difficult to handle these singularities. In the optical model proposed we wish to average over specific effects associated with individual excitation frequencies and resonances. For this purpose we consider imaginary frequencies. An imaginary-frequency perturbation simulates the actual perturbation in that its Fourier analysis contains a range of real frequencies. Physically an imaginary-frequency perturbation corresponds to

an exponentially increasing perturbation with which the target polarization does not keep pace; this too simulates the scattering situation in that a higher frequency corresponds to a faster moving electron. Mathematically the imaginary-frequency polarizability accomplishes the desired smoothing of effects associated with individual resonance frequencies in that $\alpha(i\omega)$ is a monotonically decreasing function of ω. With these motivations we now proceed to rewrite Eq. (33) in terms of frequency-dependent susceptibilities.

The basic device used to express the optical potential in terms of frequency-dependent susceptibilities is the identity[16]

$$\frac{1}{a+b}=\frac{2}{\pi}\int_0^\infty d\omega\frac{ab}{(a^2+\omega^2)(b^2+\omega^2)}\ , \tag{46}$$

where a and b are any strictly positive constants. For our applications a will be Δ_n, which is positive by definition and b will be $-V_{00}(\vec{r})$ or $E_{\text{rel}}-V_{00}(\vec{r})$. These are strictly positive for the electron-atom case considered explicitly here. For molecules these quantities can become negative for certain directions of approach of the incident electron at large r, for $-V_{00}(\vec{r})$, and at large r and very low E_{rel}, for $E_{\text{rel}}-V_{00}(\vec{r})$; the present formalism could not be applied to those cases without modification.

We will also use the identities

$$V_{0n}(\vec{r})V_{n0}''=\tfrac{1}{2}(\{[V_{n0}(\vec{r})]^2\}''-(V_{n0}')^2)-\tfrac{1}{4}V_{0n}(\vec{r})V_{n0}'''-\tfrac{1}{2}V_{0n}'V_{n0}''' \tag{47}$$

$$=-\tfrac{1}{8}\{[V_{n0}(\vec{r})]^2\}''''+\tfrac{1}{4}(V_{n0}'')^2+\tfrac{1}{4}[(V_{n0}')^2]''\ . \tag{48}$$

After a certain amount of manipulation we then obtain

$$V^{(2)}(\vec{r})=-\frac{1}{\pi}\int_0^\infty d\omega\left[\frac{-V_{00}(\vec{r})}{\omega^2+[V_{00}(\vec{r})]^2}P_0(\vec{r},i\omega)+\frac{1}{4}\left[\frac{\partial}{\partial(\omega^2)}-\frac{\omega^2-[E_{\text{rel}}+V_{00}(\vec{r})]^2}{\{\omega^2+[E_{\text{rel}}+V_{00}(\vec{r})]^2\}^2}\right]\right.$$

$$\times\left[\frac{\partial^2}{\partial r^2}P_0(\vec{r},i\omega)-P_1(\vec{r},i\omega)\right]+\frac{1}{2}\frac{\omega^2-[V_{00}(\vec{r})]^2}{\{\omega^2+[V_{00}(\vec{r})]^2\}^2}P_1(\vec{r},i\omega)\right]$$

$$-\frac{1}{4}\left[\frac{\partial}{\partial(\omega^2)}\left[-\frac{1}{2}\frac{\partial^4}{\partial r^4}P_0(\vec{r},i\omega)+\frac{\partial^2}{\partial r^2}P_1(\vec{r},i\omega)+P_2(\vec{r},i\omega)\right]\right]_{\omega=0}\ , \tag{49}$$

where

$$P_0(\vec{r},i\omega)=2\sum_n{}'\frac{|V_{n0}(\vec{r})|^2\Delta_n}{\Delta_n^2+\omega^2}\ , \tag{50}$$

$$P_1(\vec{r},i\omega)=2\sum_n{}'\frac{|V_{n0}'|^2\Delta_n}{\Delta_n^2+\omega^2}\ , \tag{51}$$

and

$$P_2(\vec{r},i\omega)=2\sum_n{}'\frac{|V_{n0}''|^2\Delta_n}{\Delta_n^2+\omega^2}\ . \tag{52}$$

Notice that differentiating $V_{n0}(\vec{r})$ with respect to r is equivalent to regarding the perturbation as

$(\partial/\partial r)^m V(\vec{r},\vec{x})$ where m is the number of differentiations. For example, for a one-electron atom with electronic coordinate $\vec{r}_1$

$$\frac{\partial}{\partial r} V(\vec{r},\vec{r}_1) = \frac{2z_1 - 2r}{|\vec{r} - \vec{r}_1|^2} , \tag{53}$$

where we have taken the z_1 axis in the direction of approach of the incident electron. Thus $P_0(\vec{r},i\omega)$ is the imaginary-frequency susceptibility to the actual perturbation, and $P_1(\vec{r},i\omega)$ and $P_2(\vec{r},i\omega)$ are imaginary-frequency susceptibilities to related perturbations.

There are several techniques for obtaining susceptibilities by the minimization of a functional.[8,10,16] The technique that seems most suitable for the present problem is that of Bartolotti and Tyrell[10] because of its flexibility for calculating dynamic polarizabilities at both real and imaginary frequencies. This generality is desirable since the present expression involves imaginary frequencies. The Bartolotti-Tyrell procedure also appears to have good numerical properties.

To calculate $P_0(\vec{r},i\omega)$ by their procedure one has to minimize the functional

$$J[\phi,S;\vec{r}] = \langle \phi | \hat{H}_{\text{int}} - \epsilon_0 | \phi \rangle + 2\langle \phi | V + S | \psi_0 \rangle$$
$$- \frac{1}{2\omega^2} \langle \psi_0 | \vec{\nabla}S \cdot \vec{\nabla}S | \psi_0 \rangle \tag{54}$$

simultaneously with respect to both $\phi(\vec{x})$ and $S(\vec{x})$ for each value of $\vec{r}$ and $\omega \geq 0$. $\vec{\nabla}S$ is a gradient in all target coordinates. Equation (54) here is completely analogous to Eq. (19) of Bartolotti and Tyrell's second paper.[11] Then by Eq. (24) of that paper

$$P_0(\vec{r},i\omega) = -2\langle \phi | V | \psi_0 \rangle . \tag{55}$$

The other susceptibilities may be calculated in a completely analogous way with V replaced by the appropriate derivative with respect to r.

IV. EFFECTIVE FREQUENCY OF THE PERTURBATION

We will define the effective frequency of the perturbation using the generalized mean-value theorem, i.e.,

$$\int_a^b d\omega \, \rho(\omega) f(\omega) = f(\omega_*) \int_a^b d\omega \, \rho(\omega) \tag{56}$$

for some $\omega_* \in (a,b)$ if $\rho(\omega) \geq 0 \ \forall \ \omega \in (a,b)$. We will also need

$$\sum_n{}' \rho_n f_n = f_* \sum_n{}' \rho_n , \tag{57}$$

with $\min f_n \leq f_* \leq \max f_n$, $n \geq 1$ if $\rho_n > 0$ for all $n \neq 0$.

Consider $V_1^{(2)}(\vec{r})$ of Eq. (30), which may also be written

$$V_1^{(2)} = -\pi^{-1} \int_0^\infty d\omega \frac{-V_{00}(\vec{r})}{[V_{00}(\vec{r})]^2 + \omega^2} P_0(\vec{r},i\omega) . \tag{58}$$

Applying Eq. (57) to Eq. (30) with

$$\rho_n = |V_{n0}(\vec{r})|^2 / \Delta_n \tag{59}$$

yields

$$V_1^{(2)}(\vec{r}) = -\left[1 - \frac{V_{00}(\vec{r})}{\Delta_*}\right]^{-1} P_0(\vec{r},\omega=0) . \tag{60}$$

Applying the generalized mean-value theorem in the form (56) to Eq. (58) with

$$\rho(\omega) = \frac{-V_{00}(\vec{r})}{[V_{00}(\vec{r})]^2 + \omega^2} \tag{61}$$

yields

$$V_1^{(2)}(\vec{r}) = -\frac{1}{2} P_0(\vec{r},i\omega_*) , \tag{62}$$

$$= -\sum_n{}' \frac{|V_{n0}(\vec{r})|^2 \Delta_n}{\Delta_n^2 + \omega_*^2} . \tag{63}$$

Applying Eq. (57) to Eq. (63) with the identification (59) yields

$$V_1^{(2)}(\vec{r}) = -\frac{1}{2} \left[1 + \left[\frac{\omega_*}{\Delta_{**}}\right]^2\right]^{-1} P_0(\vec{r},\omega=0) . \tag{64}$$

Comparing Eqs. (60) and (64) shows

$$\omega_* = [-V_{00}(\vec{r})\Delta_{**}^2 / \Delta_*]^{1/2} . \tag{65}$$

Using this in Eq. (62) shows that $V_1^{(2)}(\vec{r})$ may be interpreted as the frequency-dependent susceptibility at one frequency that depends on $\vec{r}$ through $V_{00}(\vec{r})$.

We should compare Eqs. (62) and (64) to our previous expression for $V_1^{(2)}(\vec{r})$, from Eq. (49), namely, Eq. (58). If ω_* can be estimated without actually evaluating the right-hand side of Eq. (30) or (58), then the developments of this section provide computational advantages over Eq. (58). Thus Eq. (62) requires the frequency-dependent susceptibility at only one value of the imaginary frequency, and Eq. (64) allows one to estimate this from the zero-frequency susceptibility. One way to estimate ω_* is to make the average-energy approximation. In this popular approximation Δ_n can be replaced by Δ_{av} in any sum over excited states, where Δ_{av} is approximately equal to the ionization potential or

is between the lowest-energy threshold Δ_1 and the ionization potential. Using this approximation in Eq. (65) yields

$$\omega_* = [-V_{00}(\vec{r})\Delta_{av}]^{1/2} . \tag{66}$$

Although we have explicitly considered only the $V_1^{(2)}(\vec{r})$ part of $V^{(2)}(\vec{r})$ in this section, similar considerations apply to other terms in $V^{(2)}(\vec{r})$.

In addition to the computational advantage for model studies, Eqs. (62) and (66) yield an important conceptual result, namely, they show that thinking about the scattering process in terms of a frequency-dependent susceptibility does have a foundation in more rigorous theory. The present approach shows that the second-order optical potential may be thought of as originating from the generalized frequency-dependent susceptibilities to several perturbations and their derivatives with respect to frequency and distance between the perturbers and target at several effective frequencies which change with $\vec{r}$ and the incident energy E_{rel}.

V. LOCAL-KINETIC-ENERGY APPROXIMATION

We mentioned in Sec. II that the present approximation to the second-order optical potential is only valid at low energy, and, in fact, it has the wrong high-energy limit. In this section we make a physical approximation designed to extend its range of validity. We have seen in Sec. IV that in an effective-frequency approximation the leading term of $V^{(2)}(\vec{r})$ becomes

$$V_1^{(2)}(\vec{r}) = -\sum_n{}' \frac{|V_{n0}(\vec{r})|^2 \Delta_n}{\Delta_n^2 - V_{00}(\vec{r})\Delta_{av}} . \tag{67}$$

As mentioned above this was derived as a low-energy approximation and without any consideration of exchange. At low incident energies $E \ll |V_{00}(\vec{r})|$, and if exchange is neglected, the local kinetic energy is just

$$T_{loc}(\vec{r},E_{rel}) \cong -V_{00}(\vec{r}) . \tag{68}$$

Thus we make this physical approximation in Eq. (67) and we rewrite it as

$$V_1^{(2)}(\vec{r}) \cong -\sum_n{}' \frac{|V_{n0}(\vec{r})|^2 \Delta_n}{\Delta_n^2 + T_{loc}(\vec{r},E)\Delta_{av}} . \tag{69}$$

For actual applications one would then use the approximation

$$T_{loc}(\vec{r},E_{rel}) = E_{rel} - V^{SE}(\vec{r},E_{rel}) , \tag{70}$$

where $V^{SE}(\vec{r},E_{rel})$ is a local approximation to the full static-exchange potential. Equation (70) reduces to Eq. (68) in the low-energy limit when exchange is neglected, but it is a better approximation at intermediate energy, and it has the correct high-energy limit.

Before generalizing this result, we note an ambiguity in the derivation of Sec. II. Equation (32) was motivated by the appearance and cancellation of the term $-\frac{1}{2}\sum_n{}' V_{0n}(\vec{r})V_{0n}''/\Delta_n^2$ at an earlier stage of the derivation. Based on the local-kinetic-energy model though, it might be more physical to write

$$-\sum_n{}' V_{0n}(\vec{r})V_{n0}'' \left[\frac{1}{\Delta_n^2} + \frac{2[V_{00}(\vec{r}) - E_{rel}]}{\Delta_n^3} + \cdots - \frac{1}{\Delta_n^2} \right] \cong -\sum_n{}' V_{0n}(\vec{r})V_{0n}'' \left[\frac{1}{[\Delta_n + E_{rel} - V_{00}(\vec{r})]^2} - \frac{1}{\Delta_n^2} \right] . \tag{71}$$

Using this instead of (32) in (33) shows that the general effect of resumming the series is to replace Δ_n by $\Delta_n - V_{00}(\vec{r})$ or $\Delta_n + E_{rel} - V_{00}(\vec{r})$ in the energy denominators. The local-kinetic-energy approximation recognizes this as a low-energy, no-exchange approximation to $\Delta_n + T_{loc}(\vec{r},E_{rel})$. Thus whenever one encounters Δ_n in the higher-order terms of Eq. (33), the heuristic suggestion made here is to replace it by $\Delta_n + T_{loc}(\vec{r},E_{rel})$. This presumably accounts for higher-order terms neglected by the truncation in Eq. (16). If we also make the change (71) we obtain

$$V^{(2)}(\vec{r}) = -\sum_n{}' \left[\frac{|V_{n0}(\vec{r})|^2}{\delta_n} - \frac{(V_{n0}')^2}{2\delta_n^2} + \frac{V_{0n}(\vec{r})V_{n0}''}{2\delta_n^3} - \frac{V_{0n}(\vec{r})V_{n0}''''}{4\delta_n^3} \right] , \tag{72}$$

where

$$\delta_n = \Delta_n + T_{loc}(\vec{r},E_{rel}) . \tag{73}$$

This is the final result obtained in the local-kinetic energy approximation. It may provide useful approximations at high as well as low energies.

By the arguments in Sec. IV, if one makes the local-kinetic-energy approximation then the effective frequency for the frequency-dependent-susceptibility approach becomes

$$\omega_* = \{ \, \Delta_{av}[E_{rel} - V^{SE}(\vec{r}, E_{rel})] \, \}^{1/2} \, . \tag{74}$$

Carrying out the simplications of Sec. IV with this value of ω_* reduces Eq. (72) to

$$V^{(2)}(\vec{r}) \cong \left[-\frac{1}{2} + \frac{1}{16}\frac{\partial^2}{\partial r^4} \right] P_0(\vec{r}, i\omega_*) + \left[\frac{1}{4} + \frac{1}{16}\frac{\partial^2}{\partial r^2} \right] P_1(\vec{r}, i\omega_*) - \frac{1}{8}P_2(\vec{r}, i\omega_*) \, . \tag{75}$$

In this section we have used physical arguments to remove the energy independence of some of the terms of $V^{(2)}(\vec{r})$. A second way to try to accomplish this is worth mentioning. We could have adopted a self-consistent approach instead of a strict perturbation series approach in Sec. II and written $V^{opt}(\vec{r})$ instead of $V_{00}(\vec{r})$ in Eq. (19). Then the final equations would contain the optical potential on both the left and right sides, and they would have to be solved self-consistently. This appears more rigorous, but it still does not make $V^{(2)}(\vec{r})$ tend to zero at high energy. Thus we prefer the more physical approach used in this section.

VI. SEMICLASSICAL POLARIZATION APPROXIMATION

One still finds in the literature considerable use of very simple polarization potentials like[27]

$$V^P(\vec{r}) \cong -\frac{\alpha_d}{2r^4}[1 - \exp(r/r_c)^6] \, , \tag{76}$$

where r_c is a semiempirical parameter, and where a polarization potential may be thought of as an approximation to the difference between the optical potential and the static-exchange potential, i.e.,

$$V^P(\vec{r}, E) = V^{opt}(\vec{r}, E) - V^{SE}(\vec{r}, E) \, . \tag{77}$$

The widespread use of Eq. (76) is an indication of the need for simple approximate forms of the polarization potential for applications to complicated systems. In this context we suggest a physical model based on Eq. (62) that improves on two of the most serious faults of Eq. (76). Equation (76) has first the fault that information about the target response is present only in terms of the large-r limit of the susceptibiltiy, where it reduces to the dipole polarizability divided by a power of r. Secondly it has the fault of having no energy dependence.

First we notice that $V^{(2)}(\vec{r})$ reduces to $V_1^{(2)}(\vec{r})$ in the semiclassical limit. This is seen most clearly considering Eq. (16). In the semiclassical limit the de Broglie wavelength of the scattering electron is small compared to the distances over which the potential terms change. This means that when $\hat{t}$ operates on $V_{n0}(\vec{r})f_0(\vec{r})$, $f_0(\vec{r})\hat{t}V_{n0}(\vec{r})$ is small compared to $V_{n0}(\vec{r})\hat{t}f_0(\vec{r})$. If we retain only these latter terms in the derivation of Sec. II then $V^{(2)}(\vec{r})$ reduces to $V_1^{(2)}(\vec{r})$. The semiclassical approximation involved here is similar to but not identical to the one involved in deriving the semiclassical exchange approximation.[28] Another aspect of the semiclassical exchange approximation is the local-kinetic-energy approximation. If we apply this to $V_1^{(2)}(r)$ we get

$$V^P(\vec{r}, E_{rel}) \simeq -\frac{1}{\pi}\int_0^\infty d\omega \frac{E_{rel} - V_{00}(\vec{r})}{\{ [E_{rel} - V_{00}(\vec{r})]^2 + \omega^2 \}} P_0(\vec{r}, i\omega) \tag{78}$$

$$\cong -\tfrac{1}{2}P_0(\vec{r}, i\omega_*) \, , \tag{79}$$

where (79) is equivalent to (78) if ω_* is evaluated using the generalized mean-value theorem. As a further approximation, however, we can use the average-excitation-energy approximation; then ω_* is given by Eq. (74). Using this ω_* and using Eq. (64), we can rewrite Eq. (79) as

$$V^P(\vec{r}, E_{rel}) \cong -\frac{1}{2}\left[1 + \frac{T_{loc}(\vec{r}, E_{rel})}{\Delta_{av}} \right]^{-1} P_0(\vec{r}, \omega = 0) \, , \tag{80}$$

where $T_{\mathrm{loc}}(\vec{r}, E_{\mathrm{rel}})$ is given by Eq. (70). An alternative derivation of Eq. (80) is to apply the average-excitation-energy approximation directly to Eqs. (50) and (69). The second-order approximation to the adiabatic polarization potential is[14]

$$V^{Pa}(\vec{r}) \cong -\tfrac{1}{2} P_0(\vec{r}, \omega = 0) \ . \tag{81}$$

Combining Eqs. (80) and (81) yields

$$V^{P}(\vec{r}, E_{\mathrm{rel}}) \cong \left[1 + \frac{T_{\mathrm{loc}}(\vec{r}, E_{\mathrm{rel}})}{\Delta_{\mathrm{av}}} \right]^{-1} V^{Pa}(\vec{r}) \ . \tag{82}$$

Equation (82) is similar in form to the energy-dependent polarization potential (EDPP) discussed previously,[29,30] but it seems better justified on a physical basis at small r and high E_{rel}. Because of the similarity of the derivation of Eq. (78) to the semiclassical exchange approximation, it could be called the local-kinetic-energy semiclassical polarization (SCP) approximation. Since the semiclassical exchange approximation is very successful at intermediate and high energies, the SCP approximation might also be expected to work well in those energy regimes. The SCP approximation will not give correct nonadiabatic corrections in the low-energy, large-r limit because the β and γ terms that dominate the nonadiabatic corrections there come from terms are omitted in the SCP. At low energy and large r, the EDPP of Ref. 29 should be more reliable than the SCP. But the SCP may contain the dominant contributions to the polarization effect at small r and intermediate and high energies. How quantitatively it contains these effects is a more difficult question that can be settled most clearly by actual calculations.

Equation (82) results from making the average-excitation-energy approximation as well as the semiclassical polarization approximation, and thus it would be expected to be less accurate than the full SCP approximation. Nevertheless it should be more realistic than Eq. (76), and it is in a very convenient form for applications. It also allows for the inclusion of higher-order effects by substituting a variational estimate[30,31] of $V^{Pa}(\vec{r})$ for the second-order one used in the derivation. The variational adiabatic polarization potentials are infinite-order estimates; thus they do not suffer from the important limitation that linear-response theory, used everywhere else in this article, includes only second-order effects. At small r the difference between the second-order and infinite-order estimates of $V^{Pa}(\vec{r})$ can be appreciable.

At low energy the original semiclassical approxi-

mation of Eqs. (30) and (68) is better justified than the local-kinetic-energy semiclassical approximation of Eq. (70). Thus at low energy it would be better justified to use

$$V^{P}(\vec{r}) \cong \left[1 - \frac{V_{00}(\vec{r})}{\Delta_{\mathrm{av}}} \right]^{-1} V^{Pa}(\vec{r}) \ . \tag{83}$$

than to use Eq. (82). For applications one could include the effect of exchange on the low-energy local kinetic energy by replacing V_{00} by $V^{\mathrm{SE}}(r, E_{\mathrm{rel}})$ or $V^{\mathrm{SE}}(r, E_{\mathrm{rel}} = 0)$; the latter form preserves the energy independence of the approximate polarization potential and yields

$$V^{P}(\vec{r}) \cong \left[1 - \frac{V^{\mathrm{SE}}(\vec{r}, E_{\mathrm{rel}} = 0)}{\Delta_{\mathrm{av}}} \right]^{-1} V^{Pa}(\vec{r}) \ . \tag{84}$$

It is not clear without detailed testing whether the local-kinetic-energy SCP of Eq. (82) or the low-energy SCP of Eq. (83) or (84) would yield more accurate cross sections at any given E_{rel} for a particular target.

VII. SUMMARY

The most important results of this paper are given in Eqs. (33), (49), (62), (64), (66), (72), (74), (75), (78), (82), and (83). In Sec. II we derived a low-energy approximation to the second-order optical potential. This is Eq. (33), which involves sums over a complete set of target eigenstates. In Sec. III we reexpressed Eq. (33) in terms of integrals over frequency-dependent susceptibilities with imaginary frequency. These may be calculated by standard variational techniques, and the problem of performing a sum over states of the target is thereby replaced by a simpler one. The result is Eq. (49).

Sections IV—VI discuss various modifications and extensions of the original results of Eqs. (33) and (49). Section IV discusses how the optical potential may be rewritten in terms of frequency-dependent susceptibilities at a single effective frequency; see, e.g., Eq. (62). If this frequency is then approximated physically, e.g., by the popular average-excitation-energy approximation, the calculations become much simpler; see, e.g., Eq. (64). The low-energy approximation to the modulus of the effective frequency is given by Eq. (66).

In Sec. V we physically interpret the energy denominators of the Sec. II and the effective frequency of Sec. IV. We find that these quantities involve low-energy approximations to the local kinetic energy. We replace these by more generally

applicable approximations to the local kinetic energy to extend the range of validity of the theory to cover intermediate and high energies. The resulting expressions for the second-order optical potential are Eqs. (72) and (75), and the new approximation for the effective frequency is given by Eq. (74).

In Sec. VI we discuss a further approximation to the modified theory of Sec. V, namely, a semiclassical approximation. This yields Eq. (78) if we make the local-kinetic-energy approximation and Eq. (58) if we retain the original low-energy approximation. If we make the average-excitation-energy approximation too we get a very simple result, either Eq. (82) in the local-kinetic-energy approximation or Eq. (83) in the low-energy approximation. Using these equations we can even intro-

duce higher-order terms that are neglected in the original second-order optical potential.

The results derived in this article can be applied at various levels of approximation. One important area of application is the difficult intermediate-energy regime for both electron-atom and electron-molecule scattering; for practical applications to this kind of problem, the more approximate expressions of Sec. IV — VI will probably be more useful than the more rigorous results of Secs. II and III.

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