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Exact and Semiempirical Analysis of the Generalized-Random-Phase-Approximation Optical Potential

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A many-body optical potential Σ which has been demonstrated to give excellent electron-helium elastic scattering cross sections is analyzed. It is shown to encompass, yet be more general than, almost all previous model potentials used in electron scattering and Rydberg-state calculations. A partial semiempirical form of this potential is achieved. It is shown how Σ can be computed by methods of variation-perturbation theory.

I. INTRODUCTION

The recent numerical results for the properties of the helium system by Yarlagadda *et al.*¹ show the high physical quality of the optical potential Σ , the response R , and the Martin-Schwinger one-particle Green's function G , which were computed self-consistently in the generalized-random-phase-approximation (GRPA) method postulated by Schneider *et al.*² (This paper will be referred to later in the text as STY.) These quantities immediately yielded, in simple calculations, highly accurate elastic scattering cross sections, ionization energies, generalized oscillator strengths (hence Born inelastic scattering cross sections), ground-state energies and properties, frequency-dependent moments, and moderately accurate excitation energies. In a sense these properties have all been calculated simultaneously.

The general purpose of this paper is to study the functional form of Σ given in STY (upon which the calculation of Yarlagadda *et al.*¹ is based). (Throughout this work we are implicitly assuming

that the functional form of the STY optical potential is more correct than the GRPA method that is used in the calculation.) This functional form consists of three terms [Eqs. (4.6) and (4.11a) of STY]: the Hartree-Fock term, the direct polarization term [containing the two-point response function $R(32, 3^*2^*)$], and the exchange polarization term [containing the three-point response function $R(32, 1'2^*)$]. In particular we shall seek (i) ways of using semiempirical data (on frequency-dependent moments and adsorption coefficients) in constructing Σ , and from Σ , the aforementioned properties; (ii) alternate methods of computing Σ using the excellent variation-perturbation methods of Karplus and Kolker,³ Yaris,^{4,5} and Dalgarno and Epstein⁶; (iii) to demonstrate and interpret the relation of this Σ to the multitude of optical potentials used in elastic electron-atom, -molecule scattering calculations, in the determination of Rydberg states of atoms (molecules), and for the core pseudopotentials in solids (Bethe,⁷ Temkin,⁸ Mittleman and Watson,⁹ Lippman *et al.*,¹⁰ LaBahn and Callaway,^{11,12} Khare and Shobha,¹³ Kestner

et al.,¹⁴ Eissa and Öpik,¹⁵ and Öpik,^{16,17}). (E.g., if one starts the iteration of STY with Li-atom HF orbitals, one gets properties of the Li-atom, ground-state, and *e*-Li scattering data from the Dyson equation; excitation energies come from the RPA; Σ is the optical potential. If, on the other hand one starts with the HF states of the Li⁺ ion, similar statements can be made, but one can also say that the discrete particle states will represent Rydberg states in the field of the energy-dependent, nonlocal potential of the Li⁺ ion. Here Σ contains the core polarization potential as well as the effective scattering potential.)

It shall be shown in this paper by one simple expansion (Mittleman and Watson⁹) that the present Σ encompasses the work of a large number of authors on optical potentials and pseudopotentials.

The above optical potential will be demonstrated to give completely Bethe's,⁷ LaBahn and Callaway's,¹¹ and Castillejo *et al.*'s¹⁸ potential in the adiabatic limit, with a slight modification ("cut-off") Temkin's⁸ theory.

The "orthogonality" potential of Lippmann *et al.*¹⁰ is also obtained in the adiabatic limit. The first nonadiabatic correction is derived in the form given by Mittleman and Watson,⁹ LaBahn and Callaway,¹¹ Kleinman *et al.*,¹⁹ Dalgarno *et al.*,²⁰ Khare and Shobha¹³; the associated orthogonality potential is likewise obtained. Additionally the nonadiabatic (and orthogonality) correction will be derived for the exchange polarization potential (this for the first time).

This optical potential can be used for electron scattering, for Rydberg orbitals of an atom, molecule, or ion, and also for the description of the interactions of valence electrons with the core in solids or in molecules (e.g., impurity scattering in solids). (In this paper for simplicity we deal only with closed atomic shells. Extension to other systems is tedious but not in principle new.)

As said, the here-contained analysis will allow the partial semiempirical form as well as the use of alternate (e.g., Yarlagadda *et al.*¹) methods of computing Σ_{GRPA} . These alternate procedures are not necessary to use the theory but can be convenient and theoretical unifying alternatives in many problems.

For those more familiar with the diagrammatic perturbation form of many-body theory (Kelly,²¹ Pu and Chang,²² Dutta *et al.*²³) it might well be mentioned that after iteration (renormalization) almost all important diagrams needed in the computation of the above-mentioned physical properties are represented. The difference as seen in Yarlagadda *et al.*¹ is that they are combined and weighted according to a highly physical idea. This idea is that for the calculation of small variations in Σ one can replace $\delta\Sigma$ by $\delta\Sigma_{\text{HF}}^{\text{F}}$ (superscript F

indicates the fact that only the functional form of Σ_{HF} is used). The orbitals contained in Σ are computed self-consistently and treated as unknowns. This approximation is known to give excellent results in atomic and molecular frequency-dependent-moment calculations, and its first iterate is called coupled time-dependent Hartree-Fock theory.

The plan of the paper is as follows. In Sec. II A an angular momentum analysis of the optical potential is achieved. In Sec. II B the radial part of the optical potential will be related to moments and shielding transition integrals. Section II C will use Secs. II A and II B and express Σ in a form explicitly showing the moments, shieldings, and behavior in the limits of the range of the radial variable. Section III discusses the exchange potential and Sec. IV relates Σ to previously published theories.

II. ANALYSIS OF DIRECT POLARIZATION POTENTIAL

A. Angular Momentum Analysis

The direct polarization potential [the second term in (4.6) and (4.11a) of STY] of STY can be written in the form [essentially the first two terms after Σ_{HF} in (4.11b) of STY]

$$\begin{aligned} \Sigma^{\text{dir pol}}(\vec{r}_1\vec{r}'_1; z) &= \sum_{n,k} \frac{1}{z - \omega_n - \epsilon_k} \int d\vec{r}_2 V(\vec{r}_1 - \vec{r}_2) X^{n*}(\vec{r}_2\vec{r}'_2) \\ &\quad \times \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^n(\vec{r}_3\vec{r}_3) f_k(\vec{r}_1) f_k^*(\vec{r}'_1) \\ &\quad + \sum_{n,j} \frac{1}{z + \omega_n - \epsilon_j} \int d\vec{r}_2 V(\vec{r}_1 - \vec{r}_2) X^n(\vec{r}_2\vec{r}'_2) \\ &\quad \times \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^{n*}(\vec{r}_3\vec{r}_3) g_j(\vec{r}_1) g_j^*(\vec{r}'_1), \quad (1) \end{aligned}$$

where $\omega_n = E_n - E_0$ is the excitation energy of the target system, and

$$X^n(\vec{r}, \vec{r}') = \langle 0 | \psi^\dagger(\vec{r}) \psi(\vec{r}') | n \rangle \quad (2)$$

as defined by formula (A6a) of STY; $f_k(\vec{r})$ and $g_j(\vec{r})$ are, respectively, the "particle" and "hole" Dyson orbitals with energies ϵ_k and ϵ_j ,

$$\begin{aligned} f_k(\vec{r}) &= \langle 0_N | \psi(\vec{r}) | k_{N+1} \rangle, & g_j(\vec{r}) &= \langle j_{N-1} | \psi(\vec{r}) | 0_N \rangle, \\ \epsilon_k &= E_k^{N+1} - E_0^N, & \epsilon_j &= E_0^N - E_j^{N-1} \end{aligned} \quad (3)$$

as defined with formula (A2) of STY.

It can be shown (Ref. 24) that if $|0_N\rangle$ is an S state (e.g., closed-shell target) then $X^n(\vec{r}, \vec{r}')$ can be factorized into a radial and angular part in the following way:

$$X^n(\vec{r}, \vec{r}') = X^{\text{RL}}(\gamma) Y_{LM}(\hat{r}), \quad (4)$$

where LM are the angular momentum quantum num-

bers of the state $|n\rangle$ and \bar{n} are all additional quantum numbers.

The Fourier transform of $X^n(\vec{r}, \vec{r}')$ is defined as

$$X^n(\vec{q}) = \int e^{i\vec{q}\cdot\vec{r}} X^n(\vec{r}, \vec{r}) d\vec{r}. \quad (5)$$

One can prove that (see Csanak *et al.*,²⁵ p. 305) $X^n(\vec{q})$ can be written in terms of wave functions as $X^n(\vec{q})$

$$= \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) e^{i\vec{q}\cdot\vec{r}_i} \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (6)$$

[This quantity is called the inelastic scattering form factor (Inokuti,²⁶ p. 299), and it plays an important role in the electron-atom inelastic scattering at high energies, where the Born approximation is valid (Schneider²⁷). (Therefore, it is called Born amplitude also.) In the high-energy region $|X_n(\vec{q})|^2$ "gives the conditional probability that the atom makes the transition to a particular excited state n upon receiving a momentum transfer $\hbar\vec{q}$ " (Inokuti,²⁶ p. 299). $X_n(\vec{q})$ is related to the generalized oscillator strength (GOS) introduced by Bethe²⁸ with the formula

$$f_{\bar{n}L}(q) = \frac{E_n}{Q} \sum_{M=-L}^L |X_n(\vec{q})|^2; \quad (7)$$

here E_n is the excited-state energy and $Q = \hbar^2\vec{q}^2/2m$ is the transferred energy. (Concerning the properties of GOS, see e.g., Inokuti.²⁶)

Using the partial-wave expansion of $e^{i\vec{q}\cdot\vec{r}}$ in (5) (see e.g., Bransden,²⁹ p. 10), and factorization of $X^n(\vec{r}, \vec{r}')$ in (4), one obtains

$$X^n(\vec{q}) = X^{\bar{n}L}(q) Y_{LM}(\hat{q}), \quad (8)$$

where

$$X^{\bar{n}L}(q) = 4\pi i^L \int_0^\infty r^2 j_L(qr) X^{\bar{n}L}(r) dr. \quad (9)$$

with j_L a spherical Bessel function of the first kind (Abramowitz and Stegun,³⁰ p. 437). In terms of wave functions [using (6) and (7)] we find

$$\begin{aligned} X^{\bar{n}L}(q) &= \int X^n(\vec{q}) Y_{LM}^*(\hat{q}) d\hat{q} \\ &= 4\pi i^L \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) j_L(qr_i) Y_{LM}(\hat{r}_i) \\ &\quad \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \end{aligned} \quad (10)$$

Using (8), (7) gives for the GOS

$$f_{\bar{n}L}(q) = \frac{E_n}{Q} |X^{\bar{n}L}(q)|^2 \frac{2L+1}{4\pi}. \quad (11)$$

The direct polarization potential, Eq. (1), contains $X^n(\vec{r}, \vec{r}')$ in the form of

$$V_{0n}(\vec{r}) = \int d\vec{r}' V(\vec{r} - \vec{r}') X^n(\vec{r}', \vec{r}'), \quad (12)$$

a quantity called the transition potential (Inokuti,²⁶ p. 307). Using the Bethe²⁸ form of the Coulomb

potential (in atomic units),

$$V(\vec{r} - \vec{r}') = \frac{1}{2\pi^2} \int d\vec{q} \frac{e^{i\vec{q}\cdot(\vec{r}' - \vec{r})}}{q^2}, \quad (13)$$

Eq. (12) gives [with the definition (5)]

$$V_{0n}(\vec{r}) = \frac{1}{2\pi^2} \int d\vec{q} \frac{e^{-i\vec{q}\cdot\vec{r}}}{q^2} X^n(\vec{q}), \quad (14)$$

which in turn gives via (8) (using the partial wave expansion of $e^{-i\vec{q}\cdot\vec{r}}$)

$$V_{0n}(\vec{r}) = \frac{2}{\pi} (-i)^L \int_0^\infty dq j_L(qr) X^{\bar{n}L}(q) Y_{LM}(\hat{r}). \quad (15)$$

An angular momentum factorization of the transition potential has been achieved.

Introducing the radial part of the transition potential with the definition

$$V_{0\bar{n}L}(r) = \frac{2}{\pi} \int_0^\infty dq j_L(qr) X^{\bar{n}L}(q), \quad (16)$$

Eq. (15) gives

$$V_{0n}(\vec{r}) = (-i)^L V_{0\bar{n}L}(r) Y_{LM}(\hat{r}). \quad (17)$$

It has been proven (Ref. 24) that for an S ground state the Dyson orbital can be angular momentum factorized in the form

$$\begin{aligned} f_k(\vec{r}) &= f_{n_k l_k}(r) Y_{l_k m_k}(\hat{r}), \\ g_j(\vec{r}) &= g_{n_j l_j}(r) Y_{l_j m_j}(\hat{r}). \end{aligned} \quad (18)$$

Then (1) gives, using the addition theorem for spherical harmonics (Messiah,³¹ p. 1075),

$$\begin{aligned} &\Sigma^{\text{dir pol}}(\vec{r}_1 \vec{r}'_1; z) \\ &= \sum_{\substack{\bar{n}L \\ n_k l_k}} \frac{V_{0\bar{n}L}^*(r_1) V_{0\bar{n}L}(r'_1)}{z - \omega_{\bar{n}L} - \epsilon_{n_k l_k}} f_{n_k l_k}(r_1) f_{n_k l_k}^*(r'_1) \\ &\quad \times \frac{2L+1}{4\pi} P_L(\hat{r}_1 \cdot \hat{r}'_1) \frac{2l_k+1}{4\pi} P_{l_k}(\hat{r}_1 \cdot \hat{r}'_1) \\ &\quad + \sum_{\substack{\bar{n}L \\ n_j l_j}} \frac{V_{0\bar{n}L}(r_1) V_{0\bar{n}L}^*(r'_1)}{z + \omega_{\bar{n}L} - \epsilon_{n_j l_j}} g_{n_j l_j}(r_1) g_{n_j l_j}^*(r'_1) \\ &\quad \times \frac{2L+1}{4\pi} P_L(\hat{r}_1 \cdot \hat{r}'_1) \frac{2l_j+1}{4\pi} P_{l_j}(\hat{r}_1 \cdot \hat{r}'_1). \end{aligned} \quad (19)$$

Expressing the product of Legendre functions in an expansion of the same functions (Messiah,³¹ p. 1057) (19) gives

$$\begin{aligned} &\Sigma^{\text{dir pol}}(\vec{r}_1 \vec{r}'_1; z) \\ &= \sum_{\substack{\bar{n}L \\ n_k l_k, l}} \frac{V_{0\bar{n}L}^*(r_1) V_{0\bar{n}L}(r'_1)}{z - \omega_{\bar{n}L} - \epsilon_{n_k l_k}} f_{n_k l_k}(r_1) f_{n_k l_k}^*(r'_1) \\ &\quad \times \frac{2L+1}{4\pi} \frac{2l_k+1}{4\pi} |\langle LL_k 00 | l0 \rangle|^2 P_l(\hat{r}_1 \cdot \hat{r}'_1) \\ &\quad + \sum_{\substack{\bar{n}L \\ n_j l_j, l}} \frac{V_{0\bar{n}L}(r_1) V_{0\bar{n}L}^*(r'_1)}{z + \omega_{\bar{n}L} - \epsilon_n} g_{n_j l_j}(r_1) g_{n_j l_j}^*(r'_1) \end{aligned}$$

$$\times \frac{2L+1}{4\pi} \frac{2l_i+1}{4\pi} |\langle LL_i 00 | l0 \rangle|^2 P_l(\hat{r}_1 \cdot \hat{r}_1'), \quad (20)$$

where the Clebsch-Gordan coefficient has been introduced with the notation $\langle l_1 l_2 m_1 m_2 | LM \rangle$ (see Ref. 31). An angular momentum resolution of the direct polarization part of the optical potential has been achieved. (This type of expansion is valid generally for atomic systems with *S* type of ground state; for molecules and non-*S* ground states the methods are generalizable but lengthy and will be presented as called for by their application.) For the calculation of the *S*-wave phase shift, $l=0$ has to be chosen and the radial equation should be solved. If $l=0$ is taken, then $L=l_k$ (or $L=l_j$) gives the only nonzero contribution. In this case the $L=l_k=1$ is called the dipole part, $L=l_k=2$ the quadrupole part, etc., of the optical potential.

B. Analysis of Radial Part of Transition Potential into Transition Moments and Shielding Integrals

In the following, the $L=0, 1, 2$ case of the $V_{0\bar{n}L}(r)$, the radial part of the transition potential, will be considered. It was mentioned in the Introduction that a major aim of the present analysis is that of relating the optical potential to quantities that are used in spectroscopy and can be measured directly or can be calculated with accurate methods of quantum chemistry. This program originated from Bethe²⁸ who introduced the Taylor-series expansion of $X^{\bar{n}L}(q)$ around the origin, by expanding the $j_L(qr_i)$ Bessel function into Taylor series behind the integral sign in Eq. (10). The first coefficient in this expansion is the multipole oscillator strength, a fundamental quantity in spectroscopy; the other coefficients are called hyperoscillator strengths. (These quantities will be introduced later.) From Eq. (16) it is obvious that the long-range behavior of the transition potential $V_{0\bar{n}L}(r)$ is mainly effected by $X^{\bar{n}L}(q)$'s value around $q=0$ because of the oscillatory nature of $j_L(qr)$ for large qr . Therefore, an accurate representation of $X^{\bar{n}L}(q)$ around $q=0$ gives the proper long-range behavior of $V_{0\bar{n}L}(r)$ (Inokuti,²⁶ footnote on p. 307). However, the Taylor-series expansion cannot be valid for large q (i. e., for small r in the transition potential). The physical reason for this can be seen in two ways. First, as pointed out by Inokuti,²⁶ $X^{\bar{n}L}(q)$ has to decrease rapidly because the electrons cannot obtain arbitrary momentum: "Their momentum cannot fluctuate excessively beyond a limit set by their binding." Second, the Taylor-series expansion physically means the substitution of the effect of the test charge by the first- and higher-order effects of multipole fields. However when the test charge penetrates the system (small r , large q) this physical model is not applicable, and therefore the Taylor series diverges for large-

q values. The mathematical reason that the Taylor series diverges was pointed out by Lassette,³² who used an independent particle approximation for ψ_0 and ψ_n in Eq. (10). By dividing the radial integration region to internal and external parts, he obtained for the external part the form [see Lassette,³² Eq. (14)]

$$X_e^{\bar{n}L}(q) = \int_c^\infty S_0 S_{\bar{n}} j_L dr, \quad (21)$$

($S_0, S_{\bar{n}}$ are the radial parts of the one-particle orbitals) where in this external region $S_i \sim r^{1/\alpha_i} e^{-\alpha_i r}$ is a good approximation, and $1/\alpha_i$ is the average radius of the i th state ($i=0, \bar{n}$). Taking the asymptotic form for j_L and using Euler's formula for the trigonometric function, he obtained

$$\int_c^\infty S_0 S_{\bar{n}} j_L dr = (2iq)^{-1} (e^{-iL\pi/2} F^+ - e^{iL\pi/2} F^-), \quad (22)$$

where

$$F^+ = \int_c^\infty r^\beta e^{(i\alpha - \alpha_n)r} dr, \quad (23a)$$

$$F^- = \int_c^\infty r^\beta e^{-(i\alpha + \alpha_n)r} dr, \quad (23b)$$

and

$$\beta = 1/\alpha_0 + 1/\alpha_{\bar{n}} - 1, \quad \alpha = \alpha_0 + \alpha_{\bar{n}}; \quad (24)$$

$F^+ (F^-)$ has a singularity at $q = -i\alpha$ ($i\alpha$). Now, the divergence of the Taylor series for large q is due to the fact that the $X^{\bar{n}L}(q)$ has singularities on the imaginary axis at $q = \pm i\alpha$, and therefore the radius of convergence of the Taylor series is α .

Paraphrasing for our problem the work of Lassette,³² we can introduce the representation for $X^{\bar{n}L}(q)$:

$$X^{\bar{n}L}(q) = (2iq)^{-1} (e^{-iL\pi/2} E^+ - e^{iL\pi/2} E^-) \quad (25)$$

using the $j_L(x) = \frac{1}{2}[h_L^{(1)}(x) + h_L^{(2)}(x)]$ identity, where $h_L^{(1)}(x)$ and $h_L^{(2)}(x)$ are the spherical Bessel functions of the third kind (Abramowitz and Stegun,³⁰ p. 443), and the notation

$$\begin{aligned} & \pm (iq)^{-1} e^{\pm iL\pi/2} E^{\pm(-)} \\ & = 4\pi i^L \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) h_L^{(1)(2)}(qr_i) Y_{LM}(\hat{r}_i) \\ & \quad \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \end{aligned} \quad (26)$$

From Lassette's³² work it follows that $E^{+(-)}$ has a pole at $q = -i\alpha$ ($i\alpha$), $F^{+(-)}$ being the "external" part of the integral in $E^{+(-)}$.

Now, by introducing the variable transformation $u = q/(q+i\alpha)$ in E^+ and $\bar{u} = q/(q-i\alpha)$ in E^- , the Taylor-series expansions

$$E^+ = \sum_n e_n u^n, \quad E^- = \sum_n e_n \bar{u}^n \quad (27)$$

will converge for all physical values of u (\bar{u}).

The problem is now twofold. One is to express our e_n in terms of multipole oscillator strength, hyperoscillator strengths, and/or moments of

$X^{nL}(q)$ such as

$$\int_0^\infty q^k X^{nL}(q) dq, \quad (28)$$

which gives rise to shielding oscillator strengths. (For more detailed explanation see later in this section.) (These integrals appear in shielding constants.) When this is accomplished, one can envision external electron "seeing" moments and hypermoments and an internal one probing velocity-dependent electric shieldings due to other electrons. This is an ideal physical picture for a one-particle theory. The second problem is the relation to Lassette's³² theory. Lassette³² has studied the GOS and proved that it has a pole at $q^2 = -\alpha^2$. Using the $v = q^2/(q^2 + \alpha^2)$ variable transformation he obtained a convergent Taylor-series expansion for the GOS in terms of v for all physical values of v . Now, by using the expansion (27), the Lassette expansion for the GOS can be recovered, and as such it relates our e_n 's to his expansion coefficients. Rather than develop a cumbersome notation for expressing all e_n 's in terms of Lassette's expansion coefficients, we will follow the strategy of working out in detail those terms which we claim to be physically important. In this we shall retain sufficient terms in the $X^{nL}(q)$ expansion to reproduce the minimum number of terms in the GOS expansion that Lassette³² and Vriens³³ find sufficient to fit the known helium and hydrogen data. If experience tells us we need more terms it is then a simple matter of algebra to go further. In practice, Lassette³² and Vriens³³ considered a rearranged form of the series for $F_{nL}(q)$:

for $L=0$ (Lassette)

$$F_{ns}(q) = Av(1-v)^5(1 + \sum_\nu a_\nu v^\nu), \quad (29)$$

for $L=1$ (Vriens)

$$F_{np}(q) = B(1-v)^6(1 + \sum_\nu b_\nu v^\nu), \quad (30)$$

for $L=2$ (Vriens)

$$F_{nd}(q) = Cv(1-v)^7(1 + \sum_\nu c_\nu v^\nu). \quad (31)$$

In these expansions, fitted from the helium and hydrogen data, the first factor is dominant, and the other terms are corrections to it. Guided by Lassette we now drop in the sum over ν all but the first two terms for the $L=1$ case and all terms for other L 's ($L=0, 2$). Our aim is to obtain the e_n coefficient in (27) from the (29)–(31) series. [We note that the parameter α , defined in Eq. (24), physically denoting the average inverse radius of the ground- and excited-state orbitals, depends on n . This dependence is not strong, and Lassette³² points out that "to effect the fact of convergence an error of more than 100% must be made in the estimation of α^2 ." By considering α independent of n we will not commit an error of that magnitude.]

Following what we find above, the following formulas are obtained for the form factors (from now on we use n instead of \bar{n}):

$$X^{n0}(q) \equiv X^{ns}(q) = \delta_n \frac{q^2}{(\alpha^2 + q^2)^3}, \quad (32)$$

$$X^{n1}(q) \equiv X^{np}(q) = \beta_n \frac{q}{(\alpha^2 + q^2)^3} + \gamma_n \frac{q^3}{(\alpha^2 + q^2)^4}, \quad (33)$$

$$X^{n2}(q) \equiv X^{nd}(q) = \epsilon_n \frac{q^2}{(\alpha^2 + q^2)^4}. \quad (34)$$

From these expressions one can get, using Eq. (11), the Lassette-Vriens expressions for the GOS through the terms retained, as discussed above.

We now give two methods of specifying the parameters δ_n , β_n , γ_n , and ϵ_n in terms of physical quantities. Both methods are equivalent if the exact series (27) would have been used, but one method can be favored when either physically measured data of varying physical quantities are available or when in a practical computation one intuitively feels that it is worthwhile to sacrifice short-range (long-range) accuracy to obtain better long-range (short-range) accuracy.

The first method stresses *long-range* properties. Taking the $q \rightarrow 0$ limit, Eqs. (32)–(34) give

$$X^{ns}(q) \rightarrow \frac{\delta_n}{\alpha^6} q^2, \quad (35)$$

$$X^{np}(q) \rightarrow \frac{\beta_n}{\alpha^6} q + \frac{\gamma_n}{\alpha^8} q^3 - \frac{3\beta_n}{\alpha^8} q^3, \quad (36)$$

$$X^{nd}(q) \rightarrow \frac{\epsilon_n}{\alpha^8} q^2. \quad (37)$$

Now we identify the parameters by using the exact Taylor-series expansion of $X^{nL}(q)$ around $q=0$ (Ref. 28):

$$X^{nL}(q) = \sum_{x=L}^{\infty} \frac{X_{nL}^{(x)}}{x!} q^x, \quad (38)$$

where $X_{nL}^{(x)}$'s are the spectroscopic multipole oscillator strengths. The oscillator strength is obtained for $x=L$ and [from Eq. (10)]

$$X_{nL}^{(L)} = \frac{4\pi i^L L!}{1 \cdot 3 \cdots (2L+1)} \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) r_i^L Y_{LM}(\hat{r}_i) \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (39)$$

For $L=0$ the *monopole oscillator strength* is exactly zero. For $L=1$ the *dipole oscillator strength* is obtained:

$$D_n \equiv X_{n1}^{(1)} = \frac{4}{3} \pi i \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) r_i Y_{10}(\hat{r}_i) \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (40)$$

For $L=2$ the *quadrupole oscillator strength* follows as

$$Q_n \equiv X_{n2}^{(2)} = -\frac{8}{15}\pi \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) r_i^2 Y_{20}(\hat{r}_i) \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (41)$$

For $\kappa=L+2$, the first multipole hyperoscillator strength is obtained. This is, for $L=0$, the *monopole hyperoscillator strength* is

$$F_n \equiv X_{n0}^{(2)} = -\frac{4}{3}\pi \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) r_i^2 Y_{00}(\hat{r}_i) \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (42)$$

For $L=1$ the *dipole hyperoscillator strength* is

$$H_n \equiv X_{n1}^{(3)} = -\frac{4}{5}\pi \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) r_i^3 Y_{10}(\hat{r}_i) \times \psi_n(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N. \quad (43)$$

These quantities are calculated or measured in spectroscopy. Consequently, the following identification is made:

$$\delta_n = \frac{1}{2}\alpha^6 F_n, \quad (44a)$$

$$\beta_n = \alpha^6 D_n, \quad (44b)$$

$$\gamma_n = \frac{1}{6}\alpha^8 H_n + 3\alpha^6 D_n, \quad (44c)$$

$$\epsilon_n = \frac{1}{2}\alpha^8 Q_n. \quad (44d)$$

The second method of fitting the coefficients is to realize that the dipole hyperoscillator strength may not have an important effect, and one may wish to determine γ_n to describe *short-range* penetration properly. We identify β_n as in the first method [see Eq. (44b)]; however, the second parameter is adjusted by requiring that $V_{0nP}(r)$ computed at small r [i. e., from Eq. (16), $j(qr) \approx \frac{1}{3}qr$] is the same if one uses the exact X^{nP} or, in other words, F_n given in the form of Eq. (33) provides the exact first moment

$$M_n = \int_0^\infty q X^{nP}(q) dq \quad (45)$$

by an appropriate fit for γ_n . This procedure gives γ_n as a linear combination of D_n and M_n . M_n can be written in terms of wave functions as

$$M_n = \sum_{i=1}^N \int \psi_0^*(\vec{r}_1 \cdots \vec{r}_N) \frac{1}{r_i^2} Y_{10}(\hat{r}_i) \psi_n(\vec{r}_1 \cdots \vec{r}_N) \times d\vec{r}_1 \cdots d\vec{r}_N. \quad (46)$$

The reason that we claim this gives short-range accuracy is that M_n is the key integral in the frequency-dependent dipole shielding factor which is defined as the ratio of the change of the electric

field at the nucleus due to the effect of a moving test charge to the electric field at the nucleus due to the external charge alone. (For the definition of static shielding, see, e.g., Dalgarno.³⁴)

Finally, we have, in the *first scheme*,

$$X^{nS}(q) = F_n \frac{\alpha^6 q^2}{2(\alpha^2 + q^2)^3}, \quad (47)$$

$$X^{nP}(q) = D_n \frac{\alpha^6 q}{(\alpha^2 + q^2)^3} + H_n \frac{\alpha^8 q^3}{6(\alpha^2 + q^2)^4} + D_n \frac{\alpha^6 q^3}{2(\alpha^2 + q^2)^4}, \quad (48)$$

$$X^{nD}(q) = Q_n \frac{\alpha^8 q^2}{2(\alpha^2 + q^2)^4}; \quad (49)$$

in the *second scheme* (48) is substituted for by

$$X^{nP}(q) = D_n \frac{\alpha^6 q}{(\alpha^2 + q^2)^3} - D_n \frac{2\alpha^6 q^3}{(\alpha^2 + q^2)^4} + M_n \frac{16\alpha^3 q^3}{\pi(\alpha^2 + q^2)^4}. \quad (50)$$

We repeat that for an exact representation of $X^{nL}(q)$, both schemes give identical results; however in an approximation [as (32)–(34)] the first scheme provides highly accurate long-range behavior, while the second gives good long-range and short-range behavior simultaneously for the transition potential.

C. Expression of Σ in Terms of Moments and Shieldings

We are now ready to put expressions (47)–(49) [or alternatively instead of (48), (50)] into expression (16) for the transition potential and the form so obtained into Eq. (1). Then we arrive at the following formulas for the transition potentials:

$$V_{0nS}(r) = \frac{1}{16} F_n \alpha^3 e^{-\alpha r} (\alpha r + 1), \quad (51)$$

$$V_{0nP}(r) = (D_n/r^2) \{1 - \frac{1}{8} e^{-\alpha r} [(\alpha r)^3 + 4(\alpha r)^2 + 8\alpha r + 8]\} + (\gamma_n/48\alpha^3) r e^{-\alpha r} (\alpha r + 1), \quad (52)$$

$$V_{0nD}(r) = (3Q_n/r^3) \{1 - \frac{1}{144} e^{-\alpha r} [(\alpha r)^5 + 4(\alpha r)^4 + 12(\alpha r)^3 + 42(\alpha r)^2 + 114(\alpha r) + 144]\}. \quad (53)$$

[Here γ_n is given by (44c) or by another linear expression of D_n and M_n .] Now the S-wave potential is considered as an example ($l=0$) in Eq. (20):

$$\Sigma_S^{\text{dir pol}}(r_1 r_1^1; z) = \Sigma_S^{\text{monopole}} (L=0) + \Sigma_S^{\text{dipole}} (L=1) + \Sigma_S^{\text{quadrupole}} (L=2), \quad (54)$$

where

$$\Sigma_S^L = \sum_{n, n_R} \frac{V_{0nL}^*(r_1) V_{0nL}(r_1^1)}{z - \omega_{nL} - \epsilon_{n_R L}} \times f_{n_R L}(r_1) f_{n_R L}^*(r_1^1) \left(\frac{2L+1}{4\pi}\right)^2 |\langle LL00|00\rangle|^2$$

$$+ \{\text{term containing } g_{n_j L}(r_1) g_{n_j L}^*(r'_1)\} \quad (55)$$

is the multipole contribution ($L=0, 1, 2$ gives

monopole, dipole, quadrupole, respectively) to the S-wave optical potential. Using (51)–(53) in (55) one obtains

$$\Sigma_S^{\text{monopole}} = (4\pi)^{-2} \left(\frac{1}{18} \alpha^3\right)^2 e^{-\alpha r_1} e^{-\alpha r'_1} P^{(1)}(\alpha r_1) P^{(1)}(\alpha r'_1) \left[\sum_{n_k} \mu(z - \epsilon_{n_k S}) f_{n_k S}(r_1) f_{n_k S}^*(r'_1) - \sum_{n_j} \mu(\epsilon_{n_j} - z) g_{n_j S}(r_1) g_{n_j S}^*(r'_1) \right], \quad (56)$$

$$\begin{aligned} \Sigma_S^{\text{dipole}} &= \left(\frac{3}{4\pi}\right)^2 |\langle 1100 | 00 \rangle|^2 \frac{1}{r_1^2} \frac{1}{r'_1{}^2} \left[1 - \frac{1}{8} e^{-\alpha r_1} P^{(3)}(\alpha r_1) \right] \left[1 - \frac{1}{8} e^{-\alpha r'_1} P^{(3)}(\alpha r'_1) \right] \\ &\times \sum_{n_k} \alpha_{\text{dipole}}(z - \epsilon_{n_k P}) f_{n_k P}(r_1) f_{n_k P}^*(r'_1) + \frac{1}{48\alpha^3} \left(\frac{3}{4\pi}\right)^2 |\langle 1100 | 00 \rangle|^2 \frac{1}{r_1^2} \left\{ 1 - \frac{1}{8} e^{-\alpha r_1} P^{(3)}(\alpha r_1) \right\} r'_1 e^{-\alpha r'_1} P^{(1)}(\alpha r'_1) \\ &\times \sum_{n_k} \nu(z - \epsilon_{n_k P}) f_{n_k P}(r_1) f_{n_k P}^*(r'_1) + \frac{1}{(48\alpha^3)^2} \left(\frac{3}{4\pi}\right)^2 |\langle 1100 | 00 \rangle|^2 r_1 e^{-\alpha r_1} P^{(1)}(\alpha r_1) r'_1 e^{-\alpha r'_1} P^{(1)}(\alpha r'_1) \\ &\times \sum_{n_k} \omega(z - \epsilon_{n_k P}) f_{n_k P}(r_1) f_{n_k P}^*(r'_1) + \{\text{terms containing } [g_{n_j P}(r_1) g_{n_j P}^*(r'_1)]\}, \quad (57) \end{aligned}$$

$$\begin{aligned} \Sigma_S^{\text{quadrupole}} &= \left(\frac{5}{4\pi}\right)^2 |\langle 2200 | 00 \rangle|^2 \frac{3}{r_1^3} \frac{3}{r'_1{}^3} \left[1 - \frac{1}{144} e^{-\alpha r_1} P^{(5)}(\alpha r_1) \right] \left[1 - \frac{1}{144} e^{-\alpha r'_1} P^{(5)}(\alpha r'_1) \right] \\ &\times \left[\sum_{n_k} \alpha_{\text{quadrupole}}(z - \epsilon_{n_k D}) f_{n_k D}(r_1) f_{n_k D}^*(r'_1) - \sum_{n_j} \alpha_{\text{quadrupole}}(\epsilon_{n_j D} - z) g_{n_j D}(r_1) g_{n_j D}^*(r'_1) \right]. \quad (58) \end{aligned}$$

In these formulas we find

$$P^{(1)}(x) = x + 1,$$

$$P^{(3)}(x) = x^3 + 4x^2 + 9x + 8,$$

$$P^{(5)}(x) = x^5 + 4x^4 + 12x^3 + 42x^2 + 114x + 144,$$

and we have introduced the following quantities:

$$\mu(z) = \sum_n \frac{F_n F_n^*}{z - \omega_{nS}}, \quad (59)$$

the frequency-dependent monopole hyperpolarizability;

$$\alpha_{\text{dipole}}(z) = \sum_n \frac{D_n D_n^*}{z - \omega_{nP}}, \quad (60)$$

the frequency-dependent dipole polarizability;

$$\nu(z) = \sum_n \frac{D_n \gamma_n^*}{z - \omega_{nP}}, \quad (61)$$

$$\omega(z) = \sum_n \frac{\gamma_n \gamma_n^*}{z - \omega_{nP}}. \quad (62)$$

Here γ_n is a linear combination of D_n and H_n or D_n and M_n . To calculate $\nu(z)$ and $\mu(z)$ we need to calculate the quantities (first scheme)

$$\alpha_{\text{dip-hyperdip}}(z) = \sum_n \frac{D_n H_n^*}{z - \omega_{nP}}, \quad (63)$$

$$\alpha_{\text{hyperdip}}(z) = \sum_n \frac{H_n H_n^*}{z - \omega_{nP}} \quad (64)$$

or (second scheme) the quantities

$$\gamma(z) = \sum_n \frac{D_n M_n^*}{z - \omega_{nP}}, \quad (65)$$

$$\beta(z) = \sum_n \frac{M_n M_n^*}{z - \omega_{nP}}. \quad (66)$$

In Eq. (58)

$$\alpha_{\text{quadrupole}}(z) = \sum_n \frac{Q_n Q_n^*}{z - \omega_{nD}} \quad (67)$$

is the frequency-dependent quadrupole polarizability.

Now we have achieved our objective of expressing the optical potential (at least the direct polarization term) in terms of spectroscopic quantities. Observe that as $r_1 \rightarrow \infty$ and $r'_1 \rightarrow \infty$,

$$\begin{aligned} \Sigma_S^{\text{monopole}} &\rightarrow \text{const} \times r_1 r'_1 e^{-\alpha r_1} e^{-\alpha r'_1} \sum_{n_k} \mu(z - \epsilon_{n_k S}) \\ &\times f_{n_k S}(r_1) f_{n_k S}^*(r'_1), \quad (68) \end{aligned}$$

$$\begin{aligned} \Sigma_S^{\text{dipole}} &\rightarrow \text{const} \times \frac{1}{r_1^2} \frac{1}{r'_1{}^2} \sum_{n_k} \alpha_{\text{dipole}}(z - \epsilon_{n_k P}) \\ &\times f_{n_k P}(r_1) f_{n_k P}^*(r'_1), \quad (69) \end{aligned}$$

$$\begin{aligned} \Sigma_S^{\text{quadrupole}} &\rightarrow \text{const} \times \frac{1}{r_1^3} \frac{1}{r'_1{}^3} \sum_{n_k} \alpha_{\text{quadrupole}}(z - \epsilon_{n_k D}) \\ &\times f_{n_k D}(r_1) f_{n_k D}^*(r'_1). \quad (70) \end{aligned}$$

In the adiabatic limit (see Sec. III) these formulas give

$$\Sigma_S^{\text{monopole}} \rightarrow \text{const} \times r_1^2 e^{-2ar_1} \mu \delta(r_1 - r'_1), \quad (71)$$

$$\Sigma_S^{\text{dipole}} \rightarrow \text{const} \times \frac{1}{r_1^4} \alpha_{\text{dipole}} \delta(r_1 - r'_1), \quad (72)$$

$$\Sigma_S^{\text{quadrupole}} \rightarrow \text{const} \times \frac{1}{r_1^6} \alpha_{\text{quadrupole}} \delta(r_1 - r'_1) \quad (73)$$

asymptotic forms, where α_{dipole} , $\alpha_{\text{quadrupole}}$ are the static polarizabilities and μ is the static monopole hyperpolarizability. This behavior is well known and required from any reasonable optical potential. We note that any theory that introduces quadrupole-polarization effects ($\Sigma_S^{\text{quadrupole}}$) should introduce energy dependence into the dipole-polarization part (Σ_S^{dipole}) because (as it was proved by Kleinman *et al.*¹⁹) the energy-dependent correction to the adiabatic dipole polarizability has the same long-range behavior as the quadrupole-polarization potential in the adiabatic approximation. The other limit is if $r_1 \rightarrow 0$, $r'_1 \rightarrow 0$. In this case the asymptotic behavior is obtained as

$$\Sigma_S^{\text{monopole}} \rightarrow \text{const} \times \left[\sum_{n_k} \mu(z - \epsilon_{n_k S}) f_{n_k S}(r_1) f_{n_k S}^*(r'_1) - \sum_{n_j} \mu(\epsilon_{n_j S} - z) g_{n_j S}(r_1) g_{n_j S}^*(r'_1) \right], \quad (74)$$

$$\Sigma_S^{\text{dipole}} \rightarrow \text{const} \times r_1 r'_1 \left[\sum_{n_k} \alpha_{\text{dipole}}(z - \epsilon_{n_k P}) \times f_{n_k P}(r_1) f_{n_k P}^*(r'_1) - \sum_{n_j} \alpha_{\text{dipole}}(\epsilon_{n_j P}) \times (\epsilon_{n_j P}) g_{n_j P}(r_1) g_{n_j P}^*(r'_1) \right], \quad (75)$$

$$\Sigma_S^{\text{quadrupole}} \rightarrow \text{const} \times r_1^2 r_1'^2 \times \left[\sum_{n_k} \alpha_{\text{quadrupole}}(z - \epsilon_{n_k D}) f_{n_k D}(r_1) f_{n_k D}^*(r'_1) - \sum_{n_j} \alpha_{\text{quadrupole}}(\epsilon_{n_j D} - z) g_{n_j D}(r_1) \times g_{n_j D}^*(r'_1) \right], \quad (76)$$

and in the adiabatic limit,

$$\Sigma_S^{\text{monopole}} \rightarrow \text{const} \times [\delta(r_1 - r'_1) - \rho_S(r_1 r'_1)], \quad (77)$$

$$\Sigma_S^{\text{dipole}} \rightarrow \text{const} \times r_1^2 [\delta(r_1 - r'_1) - \rho_P(r_1 r'_1)], \quad (78)$$

$$\Sigma_S^{\text{quadrupole}} \rightarrow \text{const} \times r_1^4 \{ [\delta(r_1 - r'_1) - \rho_D(r_1 r'_1)] \}. \quad (79)$$

Here $\rho_L(r_1 r'_1)$ means the multipole part of the one-particle density matrix. We would like to point out that the asymptotic behavior at large r and small r is correct, and no artificial cutoff parameter has been introduced in the optical potential as given by Eq. (54). Ultimately the calculation of the

direct polarization potential has been reduced [as can be seen from Eqs. (54)–(67)] to the calculation of frequency-dependent moments, defined by Eqs. (59)–(67).

Except for the dipole polarizability [Eq. (60)], the other moments cannot be easily measured or calculated semiempirically (e.g., by fitting sum rules, the methods of Dalgarno³⁵). Therefore, they have to be calculated. In the following only one very accurate method will be mentioned for the calculation of these quantities, namely, the variation-perturbation method (Karplus and Kolker,³ Yaris,^{4,5} Dalgarno and Epstein⁶).

In this method the equation

$$[H(1, 2, \dots, N) - z] \Phi_p(z) = p \Phi_0 \quad (80)$$

(where $\Phi_p(z)$ is essentially the dynamically perturbed state) is solved using the Hylleraas variational method (Bethe-Salpeter,³⁶ Karplus-Kolker,³ Yaris^{4,5}) to a high degree of accuracy. Basically one chooses as a basis for Φ_p , $p\Phi_0$, $[p, H]\Phi_0$, etc. This, as shown by Dalgarno and Epstein,⁶ automatically satisfies the first n sum rules and gives perturbed quantities to high accuracy. One can choose for p different operators, dipole, quadrupole, dipole-shielding, etc., perturbation, and all the mentioned quantities can be calculated. We note that in the course of this method essentially the perturbed wave function

$$\Phi_p = \sum_n \frac{\langle n | p | 0 \rangle}{\omega_n - z} \Phi_n \quad (81)$$

is calculated and with this function one obtains

$$\alpha_{\text{dipole}}(z) = \langle 0 | p | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i Y_{10}(\hat{r}_i),$$

the dipole perturbation;

$$\alpha_{\text{quadrupole}}(z) = \langle 0 | p | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i^2 Y_{20}(\hat{r}_i),$$

the quadrupole perturbation;

$$\mu(z) = \langle 0 | p | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i^2 Y_{00}(\hat{r}_i)$$

the hypermonopole perturbation;

$$\alpha_{\text{hyperdip}}(z) = \langle 0 | p | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i^3 Y_{10}(\hat{r}_i),$$

the hyperdipole perturbation;

$$\alpha_{\text{dip-hyperdip}}(z) = \langle 0 | q | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i Y_{10}(\hat{r}_i),$$

the dipole perturbation;

$$q = \sum_{i=1}^N r_i^3 Y_{10}(\hat{r}_i)$$

the hyperdipole perturbation;

$$\gamma(z) = \langle 0 | q | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N r_i Y_{10}(\hat{r}_i),$$

the dipole perturbation;

$$q = \sum_{i=1}^N \frac{1}{r_i^2} Y_{10}(\hat{r}_i),$$

the dipole-shielding perturbation;

$$\beta(z) = \langle 0 | p | \Phi_p \rangle \quad \text{if } p = \sum_{i=1}^N \frac{1}{r_i} Y_{10}(\hat{r}_i),$$

the dipole-shielding perturbation.

In summary, the direct polarization potential obtained contains monopole-, dipole-, quadrupole-polarization effects, it is energy dependent and nonlocal, at large r and small r gives the exact behavior and contains no artificial cutoff parameter. In the adiabatic limit it gives a potential that looks very similar to those used in polarized-orbital calculations (LaBahn and Callaway,¹¹ Temkin⁶).

III. ANALYSIS OF EXCHANGE POLARIZATION POTENTIAL

The exchange polarization potential is given as (STY)

$$\begin{aligned} \Sigma^{\text{exch pol}}(\vec{r}_1 \vec{r}'_1; z) &= - \sum_{n,k} \frac{1}{z - \omega_n - \epsilon_k} \int d\vec{r}_2 V(\vec{r}_1 - \vec{r}_2) X^n(\vec{r}_2 \vec{r}_2) \\ &\quad \times \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^{n*}(\vec{r}_3 \vec{r}'_1) f_k^*(\vec{r}_3) f_k(\vec{r}_1) \\ &\quad - \sum_{n,j} \frac{1}{z + \omega_n - \epsilon_j} \int d\vec{r}_2 V(\vec{r}_1 - \vec{r}_2) X^{n*}(\vec{r}_2 \vec{r}_2) \\ &\quad \times \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^n(\vec{r}'_1 \vec{r}_3) g_j^*(\vec{r}_3) g_j(\vec{r}_1). \end{aligned} \quad (82)$$

Having introduced the parametric representation of the transition potential [Eqs. (51)-(53)] the exchange polarization potential can be calculated by solving the type of equation (80) for the wave function Φ .

Let us demonstrate the procedure on the dipole term. Putting (52) into (82), because of the fact that only the parameters D_n , γ_n depend on n , one obtains the following expression [first term in (82), dipole part]:

$$\begin{aligned} &\frac{1}{r^2} \{1 - \frac{1}{8} e^{-\alpha r} [(\alpha r)^3 + 4(\alpha r)^2 + 8(\alpha r) + 8]\} \\ &\quad \times \sum_{n, n_k} \frac{D_n}{z - \omega_{nP} - \epsilon_{n_k P}} \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^{nP}(\vec{r}_3 \vec{r}'_1) \\ &\quad \times f_{n_k P}(\vec{r}_3) f_{n_k P}^*(\vec{r}_1) + \frac{1}{48\alpha^3} r e^{-\alpha r} (\alpha r + 1) \\ &\quad \times \sum_{n, n_k} \frac{\gamma_n}{z - \omega_{nP} - \epsilon_{n_k P}} \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^{nP}(\vec{r}_3 \vec{r}'_1) \end{aligned}$$

$$\times f_{n_k P}(\vec{r}_3) f_{n_k P}^*(\vec{r}_1). \quad (83)$$

Concentrating on the first term and considering the summation only on n , the following expression has to be calculated:

$$\sum_n \frac{D_n}{z - \omega_{nP} - \epsilon_{n_k P}} \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) X^{nP}(\vec{r}_3 \vec{r}'_1). \quad (84)$$

This can be written in the form

$$\begin{aligned} &\int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) \sum_n \frac{D_n \langle n | \psi^\dagger(\vec{r}_3) \psi(\vec{r}'_1) | 0 \rangle}{z - \omega_{nP} - \epsilon_{n_k P}} \\ &= \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}'_1) \langle \Phi(z - \epsilon_k) | \psi^\dagger(\vec{r}_3) \psi(\vec{r}'_1) | 0 \rangle, \end{aligned} \quad (85)$$

where $\Phi(z - \epsilon_k)$ is the solution of the first-order perturbation equation

$$(H - z + \epsilon_k) \Phi = D | 0 \rangle. \quad (86)$$

[This equation is identical to Eq. (80) if $z - z - \epsilon$ and $p = D$ (dipole perturbation) is substituted into it.]

The expression (85) contains $\Phi(z - \epsilon_k)$ in the form

$$\langle \Phi(z - \epsilon_k) | \psi^\dagger(\vec{r}_3) \psi(\vec{r}'_1) | 0 \rangle, \quad (87)$$

which can be called the transition density matrix between the state $\Phi(z - \epsilon_k)$ and the ground state of the target. This quantity can be obtained easily from the wave function $\Phi = \Phi(z - \epsilon_k)$ and Φ_0 , with the formula

$$\begin{aligned} \langle \Phi | \psi^\dagger(\vec{r}_3) \psi(\vec{r}'_1) | 0 \rangle &= N \int d\vec{\xi}_1 \dots d\vec{\xi}_{N-1} \\ &\quad \times \Phi^*(\vec{r}_3, \vec{\xi}_1, \dots, \vec{\xi}_{N-1}) \Phi_0(\vec{r}'_1, \vec{\xi}_1, \dots, \vec{\xi}_{N-1}) \end{aligned} \quad (88)$$

[analogous to Eq. (23) in Csanak *et al.*²⁵]. After having solved for Φ , this quantity can be constructed and the exchange polarization potential calculated.

For the second term in (83) the procedure is identical, only the perturbation operator in (86) is different. The monopole and quadrupole term can be handled analogously.

In summary the first-order dynamically perturbed wave function, which already has been needed for the direct polarization term, also gives the exchange polarization potential.

Note, that it is impossible to obtain any part of the exchange term from experiment. This is due to the fact that $X^n(\vec{r}, \vec{r}') = \langle 0 | \psi^\dagger(\vec{r}) \psi(\vec{r}') | n \rangle$ cannot be expanded as $X^n(\vec{r}, \vec{r})$ [or the Fourier transform of it $X^n(\vec{q})$] and physically means that a particle in exchange cannot be reproduced by any external field.

We have now completed the analysis to the degree that Σ can be obtained semiempirically. This cannot be done completely, only the dipole, quadrupole polarization and the shielding can be obtained

easily. There is little hope to obtain the cross term and less to get exchange.

It remains only to relate our potentials to that of other theories. Before doing so we would like to make two short comments.

The first is on the imaginary part of the optical potential which is needed above the first inelastic threshold. This term was not explicitly mentioned in STY and not considered in the calculation of Yarlagadda *et al.*¹ It seems to be a very small correction for elastic scattering. In principle this can be calculated once the real part of Σ is known as given previously by using the dispersion relation (Luttinger³⁷). Taking the imaginary part of the dipole polarizability, the photoionization cross section is obtained. (The authors are grateful to Dr. B. Schneider for bringing this point to their attention.)

The second is on the numerical procedure needed to compute the Dyson orbitals from Σ constructed by the aforementioned method. We note that Σ still depends on unspecified orbitals which now have to be solved for self-consistency. We can now define an iterative scheme requiring self-consistency for the Dyson orbitals (in other words for the Green's function), i. e., in the first step we use Hartree-Fock orbitals and solve for new Dyson orbitals; with these new Dyson orbitals the new optical potential is constructed and Dyson orbitals are obtained again, continuing this procedure until self-consistency is achieved. This means that the particle will polarize the core, and its own orbital will therefore change (compared to Hartree-Fock). Simultaneously the core orbitals will change, and in the next step of iteration the motion in this polarized core will be considered. Note that in the GRPA scheme the iteration for two quantities, the response function and the one-particle Green's function, has been postulated. Here only the one-particle Green's function need be determined self-consistently.

IV. DERIVATION OF PREVIOUSLY PUBLISHED THEORIES

In the following, the relationship of the general total polarization potential to other potentials used in calculations will be shown. Only the potential acting on the extra particle will be considered, i. e., the interaction potential of the extra particle with the core. This potential will not refer to the particles of the core, as before in Secs. II and III.

A. Direct Polarization Potential

Let us consider the *direct polarization potential*, as is given in Eq. (1), and let us take z in the "particle" region.

1. Adiabatic Assumption

Let us notice that under certain conditions (Mittleman and Watson,⁹ and Fetter and Watson,³⁸ pp.

129-132) the main contribution to Σ comes from those intermediate $f_k(r)$ states, for which ϵ_k is close to z (it is in "resonance" with z). For scattering this means that the scattered wave packets are made of those particle states that are near to the energy of the incoming electron. This approximation is good if "the energy fluctuations of the incident particle are small compared to those of the target" (Fetter and Watson,³⁹ pp. 129-130). The validity of the adiabatic approximation has been investigated by Mittleman and Watson.⁹ In this case the second part of $\Sigma^{\text{dir pol}}$ ("hole term") will be neglected, and in the first expression only those terms are retained that have ϵ_k energy close to z . The following expansion can be used for these terms:

$$\frac{1}{z - \omega_n - \epsilon_k} = -\frac{1}{\omega_n} \left(1 + \frac{z - \epsilon_k}{\omega_n} + \dots \right). \quad (89)$$

In the adiabatic limit only the first term will be retained in Eq. (89) and the following expression results:

$$\begin{aligned} \Sigma_{\text{adiab}}^{\text{dir pol}}(\vec{r}_1 \vec{r}'_1; z) \\ = -\sum_n \frac{V_{0n}(\vec{r}_1) V_{0n}^*(\vec{r}'_1)}{\omega_n} \sum_k f_k(\vec{r}_1) f_k^*(\vec{r}'_1). \end{aligned} \quad (90)$$

One can use the following identity (see Csanak *et al.*²⁵):

$$\sum_k f_k(\vec{r}_1) f_k^*(\vec{r}'_1) = \delta(\vec{r}_1 - \vec{r}'_1) - \rho(\vec{r}_1 \vec{r}'_1) \quad (91)$$

(this is only approximately true in our case), where $\rho(\vec{r}, \vec{r}')$ is the density matrix. (Note how the f 's have now been eliminated and the density matrix enters.)

After substituting (91) into (90) we arrive at the formula

$$\begin{aligned} \Sigma_{\text{adiab}}^{\text{dir pol}}(\vec{r}_1 \vec{r}'_1; z) \\ = -\sum_n \frac{V_{0n}(\vec{r}_1) V_{0n}^*(\vec{r}'_1)}{\omega_n} [\delta(\vec{r}_1 - \vec{r}'_1) - \rho(\vec{r}_1 \vec{r}'_1)]. \end{aligned} \quad (92)$$

The first term in this expression is the exact adiabatic polarization potential (Mittleman and Watson,⁹ Castillejo *et al.*¹⁶) as given by Bransden also [Refs. 29, p. 201, Eqs. (5-62a)-(5-62c)]. This term is the direct polarization term used in the electron-helium-atom scattering calculation of LaBahn and Callaway,¹¹ and Bethe⁷ in the He Rydberg-state calculation. Temkin's⁸ direct polarization potential can be obtained by restricting to the dipole contribution, simultaneously introducing the "cut-off" in the calculation of the transition potential $V_{0n}(\vec{r})$. Our prescription for calculating this potential is to solve the first-order adiabatically perturbed problem ($z = 0$) with the variation method.³⁶

The second term is the so-called "orthogonality

potential" (Lippman *et al.*¹⁰ and Fetter and Watson,³⁸ p. 132), after localizing the first factor. [Expanding $V_{0n}(\vec{r}_1')$ into Taylor series around \vec{r}_1 and taking the first term in this expansion, we obtain the slightly modified form of (92):

$$\sum_n \frac{V_{0n}(\vec{r}_1) V_{0n}^*(\vec{r}_1)}{\omega_n} \rho(\vec{r}_1 \vec{r}_1') \equiv V_{\text{pol}}(\nu_1) \rho(\vec{r}_1 \vec{r}_1'),$$

the expression given by Lippman *et al.*¹⁰ This type of orthogonality potential has been used successfully in the calculation of Kestner *et al.*³⁸ for e -He zero-energy scattering.

2. First Nonadiabatic Correction

The *first nonadiabatic* correction is obtained by considering the linear term in the expansion (89) from Eq. (1) which follows:

$$\begin{aligned} \Sigma_{\text{nonadiab corr}}^{\text{dir pol}}(\vec{r}_1 \vec{r}_1'; z) \\ = -\sum_n \frac{V_{0n}(\vec{r}_1) V_{0n}^*(\vec{r}_1')}{\omega_n} \sum_k (z - \epsilon_k) f_k(\vec{r}_1) f_k^*(\vec{r}_1'). \end{aligned} \quad (93)$$

Using the identity

$$h(\vec{r}) f_k(\vec{r}) = \epsilon_k f_k(\vec{r}), \quad (94)$$

where $h(\vec{r})$ is the exact one-particle operator [(94) is the Dyson equation for $f_k(\vec{r})$], (93) transforms to the form

$$-\sum_n \frac{V_{0n}(\vec{r}_1) V_{0n}^*(\vec{r}_1')}{\omega_n} [z - h(\vec{r})] [\delta(\vec{r}_1 - \vec{r}_1') - \rho(\vec{r}_1 \vec{r}_1')]. \quad (95)$$

Now we construct an equivalent potential by requiring that

$$\int \Sigma(\vec{r} \vec{r}') \psi(\vec{r}') d\vec{r}' = \int \Sigma_{\text{eq}}(\vec{r} \vec{r}') \psi(\vec{r}') d\vec{r}' \quad (96)$$

is fulfilled; then we write

$$\Sigma(\vec{r} \vec{r}') \equiv \Sigma_{\text{eq}}(\vec{r} \vec{r}') \quad (\text{equivalency}). \quad (97)$$

Substituting (95) into (96) and using the identity

$$h(\vec{r}) \psi(\vec{r}) = z \psi(\vec{r}) \quad (98)$$

[\(\psi(\vec{r})\) is a scattering state with energy z], after partial integration, one gets

$$\Sigma_{\text{nonadiab corr}}^{\text{dir pol}} = \Sigma_{\text{nonadiab corr I}}^{\text{dir pol}} + \Sigma_{\text{nonadiab corr II}}^{\text{dir pol}}, \quad (99)$$

where

$$\begin{aligned} \Sigma_{\text{nonadiab corr I}}^{\text{dir pol}}(\vec{r}_1 \vec{r}_1'; z) \\ \cong -\sum_n \frac{V_{0n}(\vec{r}_1) \vec{\nabla}_1 V_{0n}^*(\vec{r}_1)}{\omega_n} \vec{\nabla}_1 \\ - \frac{1}{2} \sum_n \frac{V_{0n}(\vec{r}_1) \vec{\nabla}_1^2 V_{0n}(\vec{r}_1)}{\omega_n}. \end{aligned} \quad (100)$$

This is the nonadiabatic correction which has been used by LaBahn and Callaway¹² in e -He scattering calculations, and is also given in this form by Khare and Shobha¹³ and, essentially, by Kleinman

*et al.*¹⁹ and Dalgarno *et al.*²⁰ (Kleinman *et al.*¹⁹ and Dalgarno *et al.*²⁰ do not obtain the first term because of different normalization of the perturbed wave function.) $\Sigma_{\text{nonadiab corr II}}^{\text{dir pol}}$ is the associated orthogonality potential to the first part in Eq. (99),

$$\begin{aligned} \Sigma_{\text{nonadiab corr II}}^{\text{dir pol}} \cong \sum_n \frac{V_{0n}(\vec{r}_1) \vec{\nabla}_1 V_{0n}(\vec{r}_1)}{\omega_n} \rho(\vec{r}_1 \vec{r}_1') \vec{\nabla}_1 \\ + \frac{1}{2} \sum_n \frac{V_{0n}(\vec{r}_1) \vec{\nabla}_1^2 V_{0n}(\vec{r}_1)}{\omega_n} \rho(\vec{r}_1 \vec{r}_1'). \end{aligned} \quad (101)$$

This nonadiabatic orthogonality term was not included in any work except those based on the Green's-function formalism (e. g., Pu and Chang²² and Yarlagadda *et al.*¹).

We can obviously derive higher nonadiabatic terms.

B. Exchange Polarization Potential

1. Adiabatic Form

The *exchange polarization potential* is given by Eq. (82). In the *adiabatic limit* [first term in Eq. (89)] the following expression is obtained:

$$\begin{aligned} \Sigma_{\text{adiab}}^{\text{exch pol}}(\vec{r}_1 \vec{r}_1'; z) \\ = \sum_n \frac{V_{0n}(\vec{r}_1) X^n(\vec{r}_1 \vec{r}_1')}{\omega_n} V(\vec{r}_1 - \vec{r}_1') - \sum_n \frac{V_{0n}(\vec{r}_1)}{\omega_n} \\ \times \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}_1') \rho(\vec{r}_3 \vec{r}_1') X^n(\vec{r}_3 \vec{r}_1'). \end{aligned} \quad (102)$$

The first part of this expression is the generalization of the exchange polarization term introduced by Temkin.⁸ [In the Hartree-Fock approximation

$$X^n(\vec{r}_1 \vec{r}_1') = \varphi_n(\vec{r}_1) \varphi_0(\vec{r}_1'),$$

where φ_n is a Hartree-Fock orbital, and the first term is written as

$$\begin{aligned} \sum_n \frac{V_{0n}(\vec{r}_1) \varphi_n(\vec{r}_1)}{\omega_n} \varphi_0(\vec{r}_1') V(\vec{r}_1 - \vec{r}_1') \\ = \chi(\vec{r}_1) \varphi_0(\vec{r}_1') V(\vec{r}_1 - \vec{r}_1'), \end{aligned}$$

where $\chi(\vec{r}_1)$ is the polarized ground-state orbital; this is the form introduced by Temkin,⁸ p. 1010.]

The second part of expression (102) is the associated "orthogonality" potential.

2. First Nonadiabatic Correction

The *first nonadiabatic correction* to the adiabatic exchange potential can be constructed similar to $\Sigma_{\text{nonadiab corr}}^{\text{dir pol}}$. Considering the second term in Eq. (89), we obtain

$$\begin{aligned} \Sigma_{\text{nonadiab corr}}^{\text{exch pol}}(\vec{r}_1 \vec{r}_1'; z) \\ = \sum_n \frac{V_{0n}(\vec{r}_1)}{\omega_n} \int d\vec{r}_3 V(\vec{r}_3 - \vec{r}_1') X^{n*}(\vec{r}_3 \vec{r}_1') \end{aligned}$$

$$\times [z - h(\vec{r}_1)] [\delta(\vec{r}_1 - \vec{r}_3) - \rho(\vec{r}_1, \vec{r}_3)] \quad (103)$$

The equivalent potential can be constructed using the identity

$$h(\vec{r}_1) \psi(\vec{r}_1) = z \psi(\vec{r}_1) \quad (104)$$

Considering the first term in (103) [that contains $\delta(\vec{r}_1 - \vec{r}_3)$],

$$\Sigma_{\text{nonadiab corr I}}^{\text{exch pol}}(\vec{r}_1, \vec{r}_1'; z)$$

$$\begin{aligned} &\cong \sum_n \frac{V_{0n}(\vec{r}_1)}{\omega_n} \{ \vec{\nabla}_1 V(\vec{r}_1 - \vec{r}_1') [\vec{\nabla}_1 + \vec{\nabla}_1'] X^n(\vec{r}_1, \vec{r}_1') \\ &+ V(\vec{r}_1 - \vec{r}_1') [\vec{\nabla}_1^2 - \vec{\nabla}_1'^2] X^n(\vec{r}_1, \vec{r}_1') \\ &+ V(\vec{r}_1 - \vec{r}_1') X^n(\vec{r}_1, \vec{r}_1') [V_{\text{eff}}(\vec{r}_1') - V_{\text{eff}}(\vec{r}_1)] \}; \end{aligned} \quad (105)$$

here V_{eff} is defined by the equation

$$h(\vec{r}) = -\frac{1}{2} \vec{\nabla}^2 + V_{\text{eff}}(\vec{r}) \quad (106)$$

Of course we do not know $V_{\text{eff}}(\vec{r})$; however, expression (105) is a very high-order correction. We can use an approximate form in (105) for V_{eff} , e. g., the Hartree-Fock expression with adiabatic polarization correction. The associated orthogonality potential can also be obtained.

Finally, let us note, that the adiabatic exchange potential can be obtained by solving the problem^{7,8}

$$[H(\vec{r}_1 \dots \vec{r}_N) - E_0] \Phi(\vec{r}_1 \dots \vec{r}_N) = \left(\sum_{i=1}^N V(\vec{r} - \vec{r}_i) + V_{\text{stat}}(\vec{r}) \right) \phi_0(\vec{r}_1 \dots \vec{r}_N) \quad (107)$$

(H is the target Hamiltonian); the first nonadiabatic correction is obtained¹³ by solving the energy-dependent problem

$$\begin{aligned} [H(\vec{r}_1 \dots \vec{r}_N) - E_0] \chi(\vec{r}_1 \dots \vec{r}_N; z) \\ = \left(-\sum_{i=1}^N V(\vec{r} - \vec{r}_i) + V_{\text{stat}}(\vec{r}) \right) \phi_0(\vec{r}_1 \dots \vec{r}_N) \\ + z \Phi(\vec{r}_1 \dots \vec{r}_N). \end{aligned} \quad (108)$$

In comparing the GRPA and the semiempirical method with Khare and Shobha's¹⁷ energy-dependent perturbation theory one can conclude that from the previous theories one can obtain the "orthogonality potential" in the adiabatic limit, whereas the energy-dependent perturbation method provides the local polarization potential, and the orthogonality potential cannot be recovered in the adiabatic limit.

It was pointed out recently³⁹ that the adiabatic theory should be used including both direct and exchange polarization. There are calculations with

the nonadiabatic corrections to the direct polarization potential; however, the nonadiabaticity of the exchange polarization potential has not been considered except in the Green's-function type of calculations. The first nonadiabatic correction to the direct adiabatic polarization potential has to be considered simultaneously with that of the exchange adiabatic potential. Let us conclude with a comment on applications to solid-state physics and diatomic molecules. The potential described herein if computed for ionic systems can clearly be used as core potentials in solid state problems. It clearly has the correct nonadiabatic orthogonality corrections. Its most useful application will probably be in impurity scattering where simple pseudopotentials have failed. (The authors thank Dr. R. Orbach for this suggestion.)

For diatomic systems one can simulate the effect of nonoverlapping distorting atomic cores by using the atomic ion potential of this paper. The problem then would be reduced to an M -electron problem, where M is the number of electrons outside the cores. For the core-core interaction one would take a van der Waals model (Dalgarno *et al.*⁴⁰) or a more sophisticated slightly overlapping core-core model as given by Yaris and Boehm.⁴¹ In any case both these corrections are completely calculable in terms of the X^{nL} 's already calculated for the atomic core potentials. This idea is a generalization of a model used by Dalgarno *et al.*,⁴⁰ and by Goddard,⁴² where in the former a semiempirically determined optical potential was employed. Öpik¹⁷ has studied the energy-dependent corrections to Rydberg core interactions in atoms and molecules.

Note added in proof. After the present manuscript had been submitted for publication a paper was published by Winifred M. Huo [J. Chem. Phys. **56**, 3468 (1972)] on a similar subject. In this paper a form is used for the transition potential which is proved here to be generally valid. Huo treats the long-range and short-range part of the transition potential separately and certain oscillatory terms are obtained for the polarization potential. A consideration of regularity at the origin of the transition potential might eliminate these oscillatory terms. (The authors are indebted to Professor Don Truhlar for bringing this paper to their attention.)

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Variational Methods for Multichannel Scattering*

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Several methods have recently been proposed for avoiding computational anomalies in the multichannel variational formalism of Kohn. The proposed methods themselves have characteristic difficulties, discussed in detail here, leading to ambiguous or discontinuous results. Two new methods are proposed. One, the optimized minimum-norm (OMN) method, is a development of the minimum-norm method of Harris and Michels. The other, the optimized anomaly-free (OAF) method, applies the idea of a preliminary unitary transformation of the open scattering channels to the anomaly-free method of Nesbet. Model calculations are reported that show both OMN and OAF methods to be superior to earlier methods. The OAF method has the additional advantage of avoiding anomalies that occur in the OMN method.

I. INTRODUCTION

The problem of spurious singularities in the Kohn variational formalism for scattering theory was first considered by Schwartz,¹ who attributed the anomalies encountered in variational calculations to singularities of the system of inhomogeneous linear equations common to all standard variational

methods. More recently, it was shown that these singularities exactly cancel out of the Kohn formulas for the tangent of the phase shift in the case of elastic scattering,² and for elements of the reactance matrix R (or K) in multichannel scattering.³ The computational anomalies result from a different aspect of the variational formalism. In both elastic and multichannel scattering the Kohn