

Polarization potential for dipole excitations

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The long-range elastic scattering from a many-electron target is due to virtual dipole excitations. For large enough partial-wave quantum number L it is a weighted sum of contributions from single-orbital dipole excitations for which the second Born approximation is valid. It is shown analytically that the corresponding potential is strictly nonlocal but is phase equivalent for large enough L to the adiabatic potential $-\alpha/2r^4$. A detailed numerical investigation is carried out for intermediate L values both of the T -matrix elements and the phase-equivalent local potential. An excellent simple approximation is found. Numerical examples involve the lowest dipole excitations of hydrogen and sodium atoms in electron scattering.

I. INTRODUCTION

The adiabatic polarization potential due to virtual dipole excitations of the target in particle scattering is, for large enough r ,

$$V_\alpha(r) = -\alpha/2r^4. \quad (1)$$

We consider the contribution to the polarization due to the dipole excitation of a target particle from an orbital ψ_{nlm} to an orbital $\psi_{n'l'm'}$. If the target is represented by the Hartree-Fock determinant this excitation is the whole excitation from the entrance channel to the corresponding dipole channel. More generally orbital excitations contribute additively to the channel excitation with coefficients given by a structure calculation.

For large enough partial-wave angular momentum L the T -matrix element T_L is given by the second Born approximation. In this case all dipole channel excitations contribute additively and our orbital excitation is typical of the general case. The breakup continuum is included in these considerations. Here $\psi_{n'l'm'}$ is replaced by the corresponding partial wave of the breakup scattering state.

We abbreviate the quantum number sets of the initial and final orbitals by the subscripts 0 and 1. The corresponding target energy eigenvalues are ϵ_0 and ϵ_1 . If $l=0$ the polarizability α for our excitation is

$$\alpha = 2\beta^2/3(\epsilon_1 - \epsilon_0), \quad (2)$$

where

$$\beta = \int_0^\infty dr r u_0(r) u_1(r), \quad (3)$$

and the radial orbitals $u_i(r)$ are given by

$$\psi_{nlm}(\mathbf{r}) = r^{-1} u_{nl}(r) Y_{lm}(\hat{\mathbf{r}}). \quad (4)$$

There has been much discussion of the polarization potential. Examples are Mittleman and Watson,¹ Vainstein,² Bonham,³ Csanak and Taylor,⁴ Byron and Joachain,⁵ and Walters.⁶ Local potentials have been proposed, which are equivalent in different senses to the

nonlocal polarization potential. In the present work we find an accurate expression for the elastic partial-wave T -matrix elements for large angular momenta and calculate the phase-equivalent local potential.

McCarthy and Stelbovics⁷ obtained some analytic results. For a given incident energy E the momentum-space potential corresponding to a local potential in coordinate space is $V(E, P)$. It depends on the absolute difference P of the momentum coordinates \mathbf{q} and \mathbf{q}' . For momentum-space potential that is analytic over the whole physical range of P the corresponding coordinate-space potential is

$$V_\alpha(E, r) = -\alpha/2r^4 + O(r^{-6}), \quad (5)$$

where α is given by

$$\alpha = 16\pi V'(E, 0). \quad (6)$$

For a dipole orbital excitation it was shown that α is given by (2) for $l=0$. The result for general angular momentum was given.

The spherical projection of the nonlocal second Born polarization potential was considered. We call this the projected local potential. It is equivalent to the nonlocal potential in the sense that it has the same Born approximation,

$$V_\alpha^{(0)}(E, P) = \frac{1}{2} \int_{-1}^1 du \langle \mathbf{q}' | V_\alpha(E) | \mathbf{q} \rangle, \quad (7)$$

$$\mathbf{P} = \mathbf{q} - \mathbf{q}', \quad u = \hat{\mathbf{q}} \cdot \hat{\mathbf{P}}, \quad q^2 = 2E. \quad (8)$$

The second Born dipole potential is anomalous, however, since the second derivative of its projected local potential is discontinuous at $P=q \pm x$, where x is the momentum of the particle in the dipole channel

$$x^2 = q^2 + 2(\epsilon_0 - \epsilon_1). \quad (9)$$

Note that x is imaginary below the excitation threshold. It follows that the projected local potential has the form (5) in this energy range.

For incident energy above the excitation threshold the projected local potential has the form

$$V_{\alpha}^{(0)}(E, r) = -\frac{1}{2r^4} \left[\alpha + \frac{3g(0)g(q-x)\cos[(q-x)r]}{q(q-x)} + \frac{3g(0)g(q+x)\cos[(q+x)r]}{q(q+x)} \right], \quad (10)$$

where

$$g(k) = k^{-1} \int_0^{\infty} dr j_1(kr) u_0(r) u_1(r), \quad (11)$$

$$g(0) = \beta/3.$$

This gives an energy-dependent oscillation about the adiabatic form for all values of r .

McCarthy and Stelbovics confined their discussion to the projected local potential. No statements could be made about the phase-equivalent local potential. However, the disagreement of (5) and (10), due to a rather subtle anomaly in $V_{\alpha}^{(0)}(E, P)$, warns us to be careful of general arguments. We therefore study the structure of the second Born T -matrix element carefully and compute it to an accuracy of four significant figures for large L for which it is mainly real. We find a simple approximation, whose validity increases with L , which agrees exactly with the first Born approximation to the T -matrix elements of (1).

II. THE T -MATRIX ELEMENT FOR LARGE L

For large enough partial-wave angular momentum L the elastic T -matrix element T_L for a dipole excitation is essentially real and obeys the second Born approximation. We consider L large enough for departures from both these criteria to be negligible. At such angular momenta a weaker condition is also satisfied. The static and exchange potential matrix elements are negligible. The relevant formalism has been given by McCarthy and Stelbovics,⁸

$$T_L = 2 \int_0^{\infty} dk \frac{1}{x^2 - k^2} \times \{ k^2 [V_L^{(+)}(q, k)]^2 + k^2 [V_L^{(-)}(q, k)]^2 - x^2 [V_L^{(+)}(q, x)]^2 - x^2 [V_L^{(-)}(q, x)]^2 \}. \quad (12)$$

Note that if T_L is real then the on-shell potential matrix elements $V_L^{(\pm)}(q, x)$ are negligible. The potential matrix elements $V_L^{(\pm)}(q, k)$ are special cases for dipole excitations of⁸

$$V_{nLl}^{n'L'l'(J)}(q, k) = \sum_{\lambda} \frac{2}{\pi q k} (-)^{l+l'+J} \begin{Bmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} L & L' & \lambda \\ 0 & 0 & 0 \end{Bmatrix} \times \begin{Bmatrix} l & L & J \\ L' & l' & \lambda \end{Bmatrix} \hat{L} \hat{L}' \hat{\Pi}' R_{LL'}^{(\lambda)}(q, k). \quad (13)$$

The factor $i^{L-L'}$ is absorbed in the definition of the partial-wave T -matrix element.

We choose $l=0, l'=\lambda=1, J=L, L'=L\pm 1$. The corresponding special values of the $3j$ and $6j$ symbols in (13) are

$$\begin{Bmatrix} 0 & L & L \\ L\pm 1 & 1 & 1 \end{Bmatrix} = [3(2L+1)]^{-1/2},$$

$$\begin{Bmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \end{Bmatrix} = 3^{-1/2},$$

$$\begin{Bmatrix} L & 1 & L+1 \\ 0 & 0 & 0 \end{Bmatrix} = (-1)^{L+1} \left[\frac{L+1}{(2L+1)(2L+3)} \right]^{1/2},$$

$$\begin{Bmatrix} L & 1 & L-1 \\ 0 & 0 & 0 \end{Bmatrix} = (-1)^L \left[\frac{L}{(2L-1)(2L+1)} \right]^{1/2}, \quad (14)$$

and

$$\hat{L} = (2L+1)^{1/2}. \quad (15)$$

The potential matrix elements are

$$V_L^{(+)}(q, k) = \frac{2}{\pi q k} \left[\frac{L+1}{3(2L+1)} \right]^{1/2} R_L^{(+)},$$

$$V_L^{(-)}(q, k) = \frac{2}{\pi q k} \left[\frac{L}{3(2L+1)} \right]^{1/2} R_L^{(-)}, \quad (16)$$

where

$$R_L^{(\pm)}(q, k) = \beta(qk)^{1/2} (\pi/2) \int_0^{\infty} dr r^{-1} J_{L+1/2}(qr) \times J_{L\pm 1+1/2}(kr), \quad (17)$$

and β is given by (3). Substituting these values in (12) gives

$$T_L = \frac{2}{3} \left[\frac{2}{\pi q} \right]^2 \int_0^{\infty} dk \frac{1}{x^2 - k^2} \frac{1}{2L+1} \times [(L+1)R_L^{(+)^2} + LR_L^{(-)^2}]. \quad (18)$$

The quantities $R_L^{(\pm)}$ may be evaluated analytically using the identity⁹

$$\int_0^{\infty} dr r^{-1} J_{\nu}(\alpha r) J_{\mu}(\beta r) = \frac{1}{2} \left[\frac{\alpha}{\beta} \right]^{\nu} \frac{\Gamma((\nu+\mu)/2)}{\Gamma(1-(\nu-\mu)/2)\Gamma(\nu+1)} \times F \left[\frac{\nu+\mu}{2}, \frac{\nu-\mu}{2}, \nu+1; \frac{\alpha}{\beta} \right], \quad (19)$$

where $\alpha < \beta$ and F is the hypergeometric function. The k integration may then be evaluated numerically.

The function $[(L+1)R_L^{(+)^2} + LR_L^{(-)^2}]$ in the integrand of (18) is strongly peaked at $k=q$ for large L and peaks more strongly as L increases. The reason for this is the factor $(\alpha/\beta)^{\nu}$ for $\alpha < \beta$ in the identity (19), which becomes $(k/q)^{\nu}$ for $k < q$ and $(q/k)^{\nu}$ for $k > q$. We make

the following approximation to obtain an estimate $T_L^{(1)}$ of T_L :

$$T_L^{(1)} = \frac{2}{3} \left[\frac{2}{\pi q} \right]^2 \frac{1}{x^2 - q^2} \times \int_0^\infty dk \frac{1}{2L+1} [(L+1)R_L^{(+)} + LR_L^{(-)}]. \quad (20)$$

We may evaluate this expression analytically⁹ using the orthonormality relation for Bessel functions of half-integer order,

$$\int_0^\infty dk k J_{n+1/2}(kr) J_{n+1/2}(kr') = \delta(r-r')/r. \quad (21)$$

The relevant integral has the same value for $n=L\pm 1$, namely,

$$\int_0^\infty k dk \int_0^\infty dr \int_0^\infty dr' (rr')^{-1} J_{L+1/2}(qr) J_{L+1/2}(qr') J_{L\pm 1+1/2}(kr) J_{L\pm 1+1/2}(kr') = \int_0^\infty dr r^{-3} J_{L+1/2}(qr) J_{L+1/2}(qr) = \frac{q^2}{2^3} \frac{\Gamma(3)\Gamma(L-1/2)}{\Gamma(2)\Gamma(L+5/2)\Gamma(2)} = \frac{2q^2}{(2L+3)(2L+1)(2L-1)}. \quad (22)$$

Using (2), (9), (17), and (20) we have the following expression for $T_L^{(1)}$:

$$T_L^{(1)} = \frac{-\alpha q}{(2L+3)(2L+1)(2L-1)}. \quad (23)$$

Equation (23) for $T_L^{(1)}$ is identical to the Born approximation T -matrix element for scattering by the local adiabatic potential (1),

$$T_L^{(1)} = \int d\hat{q}' \int d\hat{q} \sum_M Y_{LM}(\hat{q}') Y_{LM}^*(\hat{q}) \langle \mathbf{q}' | V_\alpha | \mathbf{q} \rangle = \frac{-\alpha}{2q} \int dr r^{-3} J_{L+1/2}(qr) J_{L+1/2}(qr). \quad (24)$$

Using (22) this is seen to be identical to (23).

Here we have rederived the first-order result of O'Malley, Spruch, and Rosenberg.¹⁰ Their result for the first-order phase shift $\delta_L^{(1)}$ is given by

$$T_L^{(1)} = \frac{-1}{\pi q} \tan \delta_L^{(1)}. \quad (25)$$

Here we have assumed that L is so large that $T_L^{(1)}$ is essentially real. This is the same as the condition for validity of the Born approximation.

It is possible to understand the variation of T_L , given by (18), with x^2 analytically. We first consider T_L at the dipole-excitation threshold $x^2=0$. We do the k integration using the identity

$$\int_0^\infty dk k^{-1} J_{n+1/2}(kr) J_{n+1/2}(kr') = (2n+1)^{-1} (r_</r_>)^{n+1/2}, \quad (26)$$

which is a special case of (19). Here $r_<$ and $r_>$ are the lesser and greater of r and r' , respectively. The r integration is then done by a further application of this identity, leaving a simple integration over a new variable $z=r'/r$. The derivation is outlined below,

$$\begin{aligned} & \int_0^\infty dk k^{-1} \int_0^\infty dr \int_0^\infty dr' (rr')^{-1} J_{L+1/2}(qr) J_{L+1/2}(qr') [(L+1)J_{L+3/2}(kr) J_{L+3/2}(kr') + L J_{L-1/2}(kr) J_{L-1/2}(kr')] \\ &= \int_0^\infty dr r^{-1} \int_0^1 dz z^{-1} J_{L+1/2}(qr) J_{L+1/2}(qzr) \left[\frac{L+1}{2L+3} z^{L+3/2} + \frac{L}{2L-1} z^{L-1/2} \right] \\ &+ \int_0^\infty dr r^{-1} \int_1^\infty dz z^{-1} J_{L+1/2}(qr) J_{L+1/2}(qzr) \left[\frac{L+1}{2L+3} z^{-L-3/2} + \frac{L}{2L-1} z^{-L+1/2} \right] \\ &= \frac{2}{(2L+3)(2L-1)}. \end{aligned} \quad (27)$$

We now substitute (26) in (18) using (17) and use (2) and (9) to obtain once again the expression (23) for T_L .

T_L is therefore exactly equal to $T_L^{(1)}$ at the threshold $x^2=0$. We now consider the expression (18) for T_L and note that $(k^2-x^2)^{-1}$ is less than k^{-2} for $x^2<0$ and greater than k^{-2} for $x^2>0$. $T_L/T_L^{(1)}$ is therefore greater than 1 for $x^2>0$ (above threshold) and less than 1 for $x^2<0$ (below threshold).

III. NUMERICAL EVALUATION OF THE APPROXIMATION $T_L = T_L^{(1)}$

In order to assess the approximation $T_L = T_L^{(1)}$ we consider the difference

$$T_L - T_L^{(1)} = \frac{2}{3} \left[\frac{2}{\pi q} \right]^2 \int_0^\infty dk \frac{k^2 - q^2}{(x^2 - k^2)(x^2 - q^2)} \frac{1}{2L+1} [(L+1)R_L^{(+)} + LR_L^{(-)}]. \quad (28)$$

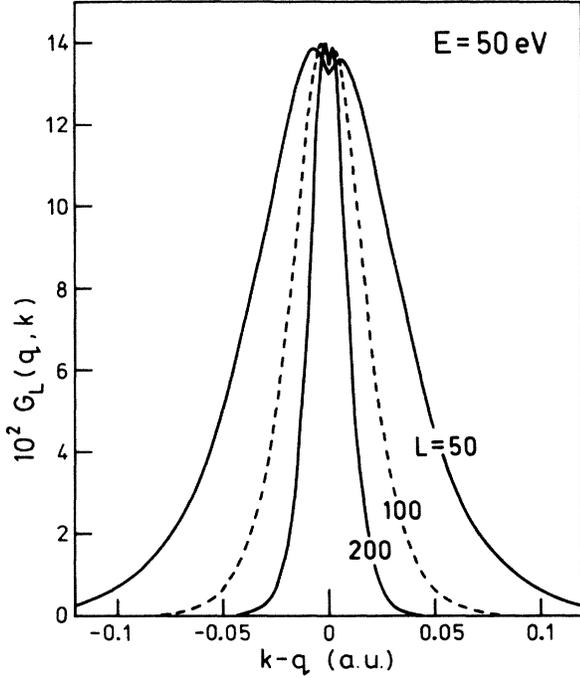


FIG. 1. The function $G_L(q, k)$ of Eq. (25) plotted against $k - q$ for different L values at 50 eV.

The first factor in the integrand is antisymmetric in k and q .

In Fig. 1 we have plotted the dimensionless quantity

$$G_L(q, k) = (2/\pi k)^4 (q/\beta)^2 [(L+1)R_L^{(+)} + LR_L^{(-)}] \times \left[\frac{L+1}{(2L+1)^2} + \frac{L}{(2L-1)^2} \right]^{-1} \quad (29)$$

for $E = 50$ eV. G_L is characteristic of dipole scattering but independent of the particular target structure. It is strongly peaked about $k = q$ and almost symmetric. It becomes more peaked and more symmetric as L increases.

$G_L(q, k)$ is approximately a universal function for dipole scattering in the sense that the relation

$$G_{\gamma L}(\gamma q, k) = G_L(q, k) \quad (30)$$

is very nearly obeyed. This relationship holds within about 10% over the range $\gamma = 1$ to 10 starting for example with $E = 20$ eV, $L = 20$ or $E = 20$ eV, $L = 40$. T_L therefore approaches $T_L^{(1)}$ as L increases. The relative difference for different values of L is given approximately by

$$T_{\gamma L}(\gamma q)/T_{\gamma L}^{(1)}(\gamma q) - 1 = \gamma^2 [T_L(q)/T_L^{(1)}(q) - 1]. \quad (31)$$

IV. DISCUSSION WITH NUMERICAL EXAMPLES

The first-order term of the second Born T -matrix element for elastic scattering with a single-orbital dipole excitation (23) is identical with the Born approximation to

the scattering by the adiabatic potential. The potentials are therefore phase equivalent in these approximations. Since the Born approximation tends to the correct potential scattering T -matrix element for large L we may regard the form $T_L^{(1)}$ as the large- L form of the adiabatic T -matrix element, corresponding to large r in the local potential. In this sense r is large when $r^{-6} \ll r^{-4}$.

It is interesting to evaluate the electron elastic scattering T -matrix element numerically using the expression (18) in its range of validity. This is determined from a coupled-channels calculation using the criteria that L is large enough for the second Born approximation to be within 1% of the correct T_L and that the imaginary part of T_L is less than 1% of the real part. The minimum L in the range is called L_0 .

We are interested first in the way in which T_L tends to $T_L^{(1)}$ as L increases. Figure 2 shows the quantity $(T_L/T_L^{(1)} - 1) \times 10^2$ for the hydrogen 1s, 2p excitation ($\alpha = 2.9596$, $\epsilon_1 - \epsilon_0 = 10.2$ eV) and for sodium 3s, 3p using Hartree-Fock orbitals ($\alpha = 176.63$, $\epsilon_1 - \epsilon_0 = 2.1$ eV). For $E = \epsilon_1 - \epsilon_0$, i.e., at the excitation threshold $x^2 = 0$, $T_L = T_L^{(1)}$ for all $L \geq L_0$. For negative values of x^2 , $T_L > T_L^{(1)}$. As E increases T_L and $T_L^{(1)}$ differ more widely. The approximate validity of (31) is verified. Table I shows the distance R , defined by

$$R = L_1/q, \quad (32)$$

where L_1 is the angular momentum value beyond which T_L is within 1% of $T_L^{(1)}$. We may consider R as the minimum distance at which the nonlocal polarization

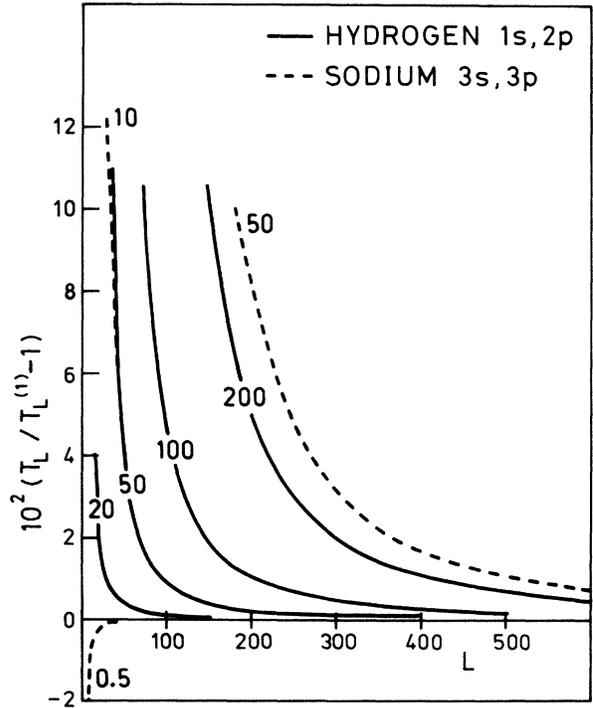


FIG. 2. The quantity $(T_L/T_L^{(1)} - 1) \times 10^2$ plotted against L for electron elastic scattering from hydrogen 1s, 2p and sodium 3s, 3p at the indicated incident energies E (eV).

TABLE I. The distance $R=L_1/q$, where L_1 is the angular momentum value beyond which T_L is within 1% of $T_L^{(1)}$ for the indicated electron elastic scattering reactions.

Target	E (eV)	L_1	R (a.u.)
H 1s,2p	20	28	23.1
	50	94	49.0
	100	206	76.0
	200	420	109.5
Na 3s,3p	10	94	109.6
	50	522	272.3

potential is phase equivalent to the adiabatic potential (1). R increases with E . For the hydrogen 1s,2p excitation R is 23.1 a.u. for $E=20$ eV and 109.5 a.u. at 200 eV. At 50 eV R is 49.0 a.u. for hydrogen 1s,2p, but it increases to 272.3 a.u. for the much more polarizable sodium 3s,3p case.

V. THE PHASE-EQUIVALENT LOCAL POTENTIAL

The phase-equivalent local potential for elastic scattering may be obtained by inverting the phase shifts using the WKB approximation¹¹ with the following analytic expression for the S -matrix elements:¹²

$$S_L(\mathbf{a}) = \prod_{n=1}^N \frac{\lambda^2 - \beta_n^2}{\lambda^2 - \alpha_n^2}, \quad (33)$$

$$\lambda = L + \frac{1}{2}. \quad (34)$$

The vector \mathbf{a} represents the set of $2N$ complex parameters α_n, β_n determined by fitting $2N$ complex phase shifts. The expression (33) usually interpolates a set of phase shifts accurately to within a few percent.

The inverted potential is

$$V(\rho) = E[1 - \exp(-Q(\sigma)/E)], \quad (35)$$

where

$$\rho = qr = \sigma \exp[Q(\sigma)/2E], \quad (36)$$

and the quasipotential $Q(\sigma)$ is given by

$$Q(\sigma) = \frac{4E}{\pi} \frac{1}{\sigma} \frac{d}{d\sigma} \int_{\sigma}^{\infty} d\lambda \frac{\delta(\lambda)}{(\lambda^2 - \sigma^2)^{1/2}} \\ = 2iE \sum_{n=1}^N \left[\frac{1}{(\sigma^2 - \alpha_n^2)^{1/2}} - \frac{1}{(\sigma^2 - \beta_n^2)^{1/2}} \right], \quad (37)$$

and

$$S_\lambda = \exp(2i\delta_\lambda). \quad (38)$$

We have inverted the set of complex phase shifts obtained up to L_0 by solving the hydrogen 1s,2p coupled-channels problem⁸ and for larger values of L by using the expression (18). Ten complex phase shifts were fitted at 50 and 200 eV for the following L -values: for 50 eV,

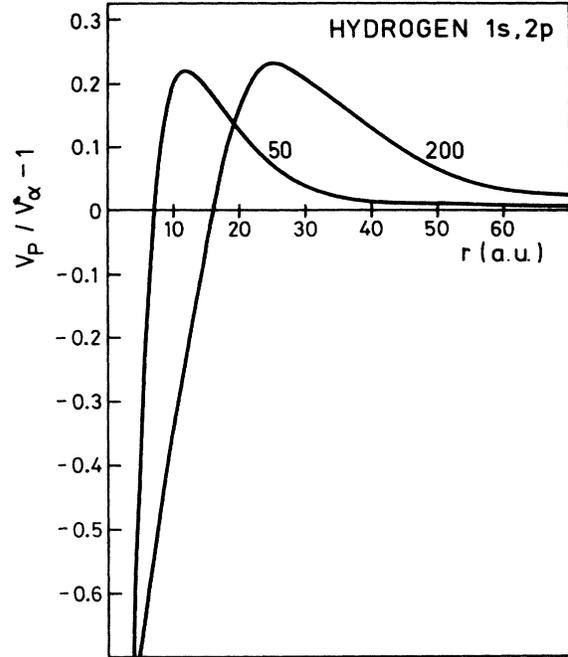


FIG. 3. The phase-equivalent local potential $V_p(r)$ for electron elastic scattering from the hydrogen 1s,2p system plotted at $V_p/V_\alpha - 1$ for comparison with the adiabatic potential (1) at the indicated energies E (eV).

$$L = 0, 1, 2, 5, 10, 34, 50, 100, 150, 196 \quad (L_0 = 34),$$

and for 200 eV,

$$L = 0, 1, 2, 5, 10, 30, 70, 136, 140, 160 \quad (L_0 = 136).$$

The phase-equivalent real local polarization potential $V_p(r)$ is compared with the adiabatic potential (1) in Fig. 3, where $V_p/V_\alpha - 1$ is plotted against r for 50 eV and 200 eV. $V_p(r)$ is obtained from the inverted potential of (35) by subtracting the static potential and the equivalent local exchange potential of Furness and McCarthy.¹³ The static exchange potential is negligible at the 1% level beyond $r=7$ a.u. at both energies.

VI. CONCLUSIONS

We have considered the phase equivalence of the non-local potential for elastic scattering with dipole excitations, the projected local potential and the adiabatic potential $-\alpha/2r^4$ in two radial regions. For incident energy $E=q^2/2$ the radial regions are $L_0 < qr < L_1$ and $qr > L_1$. L_0 is the minimum partial-wave angular momentum for which the approximations of this work are valid at the 1% level. The basic approximation is Eq. (18) for the elastic T -matrix element T_L . At $L=L_0$, T_L is essentially real, it is given essentially by the second Born approximation to the coupled-channels problem, the first Born approximation for inelastic channels is valid, the first Born approximation to scattering from the adiabatic potential is valid, and the contribution to T_L from the static exchange potential vanishes.

Note that L_0 is considerably reduced if we relax the condition that T_L is real. The imaginary part corresponding to (18) is of course simple to calculate. For sodium $3s, 3p$ at 50 eV, for example, the other criteria are satisfied at the 1% level for $L=30$, while T_L does not become real until $L=196$.

We have shown analytically that the nonlocal polarization potential is phase equivalent to the adiabatic potential for large enough r . This follows from the fact that T_L tends to $T_L^{(1)}$ [Eq. (23)] as L increases. L_1 is the value of L for which T_L first approaches to within 1% of $T_L^{(1)}$.

A real target has thresholds for many different discrete and continuum dipole excitations. We have discussed the excitation of one dipole channel, which is typical of all channels when the second Born approximation is valid. At energies greater than the first dipole threshold the projected local potential is never the same as the polarization potential, since it has an oscillating form for $qr > L_1$. Below the first excitation threshold these two potentials are the same for $qr > L_1$ and they are both equal to the adiabatic potential.

For $L > L_0$ the elastic T -matrix element T_L for a single excitation is less than $T_L^{(1)}$ below the threshold, equal to $T_L^{(1)}$ at the threshold, and greater than $T_L^{(1)}$ above the

threshold. The corresponding inequalities exist for the comparison of the phase-equivalent and adiabatic local potentials. The phase-equivalent local potential is up to 20% larger than the adiabatic potential at several atomic radii for electron-atom scattering at higher energies.

The easily evaluated expression (18) is an excellent approximation to T_L for $L > L_0$. The full coupled-channels calculation needs to be done only for $L \leq L_0$. For inelastic channels the partial-wave T -matrix elements are given by the Born approximation for $L > L_0$, so the three-dimensional T -matrix element may be evaluated⁸ to all L by using the analytic Born approximation for $L > L_0$. This method, however, is not applicable to the elastic T -matrix element because it never obeys the Born approximation if there are dipole channels. For $L \sim L_0$ (18) gives an excellent check on the numerical methods used for solving the coupled-channels problem.

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