Dominant Nonadiabatic Contribution to the Long-Range Electron-Atom Interaction*†

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(Received 10 July 1967; revised manuscript received 13 December 1967)

In the scattering of low-energy electrons or positrons by spherically symmetric atoms, a significant role is played by the long-range interactions. These originate partially in the adiabatic polarization of the atom, which contributes $1/q^4$, $1/q^6$, and higher terms, where q is the electron-atom separation. There is also a nonadiabatic contribution, which behaves asymptotically as $3a_0\beta_1(e')^2/q^6$, where e' is the charge of the incident particle; this contribution was first studied by Mittleman and Watson in the case of hydrogen. We have obtained a useful if formally trivial extension of their results on β_1 to a wide class of atoms. We have also obtained rigorous if sometimes crude upper and lower bounds on β_1 which depend upon the availability of some information on the low-lying atomic energy levels and the associated oscillator strengths, and on the electric dipole polarizability. Bounds on β_1 have been obtained for He, Li, Ne, and Na. Statistical moment studies lead to estimates of β_1 for the rare-gas atoms.

1. INTRODUCTION

THE problem of the scattering of low-energy electrons by complex atoms is clearly not one that can readily be attacked theoretically from first principles. In fact, the presence of significant effective long-range potentials causes the phase shifts to vary so rapidly with the energy that it is difficult, even using experimental data, to extrapolate or interpolate in a study of the phase shifts as functions of the energy unless one explicitly extracts long-range effects.

It was recognized some time ago[1] that effective-range theory as originally introduced in nuclear physics was not directly applicable to the scattering of charged particles by neutral polarizable systems, and a modified effective-range theory was introduced[1,2] in which the contributions of the long-range interactions which can, at least in principle, be deduced from experimental data are separated out. The short-range interactions cause a relatively slow variation of the phase shifts with energy; for each phase shift, this effect can often be adequately characterized, in the domain from zero to a few eV, by two parameters, analogs of the scattering length and effective range of the usual effective-range theory. This combination of a theoretical analysis of long-range effects which extracts the rapidly varying component of the energy dependence, a component which is not an analytic function, and the subsequent theoretically well-founded phenomenological analysis of the short-range effects can be particularly useful in determining the scattering in the very low energy domain largely inaccessible to the experimentalist. Modified effective-range theory has been applied to the scattering of low-energy electrons by hydrogen atoms[3] and by the rare gases.[4]

The original papers[1,2] and the applications[3,4] contained an analytic study of the dominant effects of the polarization potential which varies as $1/q^4$, where q is the distance between the incident charged particle and the atom; long-range effects were not fully accounted for. More generally, the point was stressed that all long-range potentials have their somewhat unusual energy-dependent effects precisely because of the contribution that comes from very great distances; since the potential is exceedingly weak there, the specifically long-range contribution to the phase shift is given *exactly* by the Born expansion. More precisely, all contributions to the phase shift η_L associated with angular momentum L which dominate over the k^{2L+1} short-range contribution are given *exactly* by the Born expansion connected with the long-range interaction.[5] For higher values of L, and particularly for large values of the electric dipole polarizability α_1 of the target, where higher terms in the Born expansion—which are very difficult to obtain analytically—may still be more important than short-range effects, it is useful to determine long-range effects numerically; one should be perfectly happy to solve a one-body problem numerically if it is useful in the analysis of a many-body problem. The formulation of the numerical problem has been given not only for neutral-atom targets[6] but for charged-ion targets.[7] (The

* The work reported on in this article was sponsored by the U. S. Office of Naval Research, the Advanced Research Projects Agency under Contract No. Nonr-285(49), NRO12-109, and NASA under Contract No. NSG 699.

† Preliminary reports were given at the New York meeting of the American Physical Society in June 1965 [Bull. Am. Phys. Soc. **10**, 584 (1965)] and at the *Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, USSR, July 1967* (Publishing House, Nauka, Leningrad, USSR), p. 276.

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latter formulation is also applicable to the scattering of charged particles by nuclei.) Tables of coefficients for the $1/q^4$ case, as functions of the energy, for various target electric dipole polarizabilities and for different orbital angular momenta, should be available soon[8]; the effect of the $1/q^6$ term can often be treated via perturbation theory. The determination of the coefficient of the $1/q^6$ term forms the subject of the present paper.

The analysis of the effects of long-range potentials obviously requires a knowledge of the dominant terms in that potential. For the scattering of a light incident particle of charge e' by a (fixed) nucleus of charge Ze containing z electrons, the long-range interaction will be shown to be

$$V(q)=\frac{(Z-z)ee'}{q}-\frac{\alpha_1(e')^2}{2q^4}-\left(\frac{\alpha_2}{2}-3a_0\beta_1\right)\times\frac{(e')^2}{q^6}+O\left(\frac{1}{q^7}\right). \quad (1.1)$$

$a_0=\hbar^2/me^2$ is the Bohr radius, α_1 and α_2 are the electric dipole and quadrupole polarizabilities, respectively, of the atom or ion, and β_1 determines the leading nonadiabatic correction, a measure of the inability of the electric dipole induced in the target to follow the motion of the incident particle. A precise (formal) definition of β_1 will be derived, and estimates of β_1 for a few atoms will be given. The leading nonadiabatic contribution was first obtained by Mittleman and Watson[9] for the case of e^-H scattering; it was in non-Hermitian form. An equivalent Hermitian form[10] was subsequently obtained by Mittleman. The parameters α_1, α_2, and β_1 are properties of the target only; they are independent of the particle being scattered. A review of the available theoretical and experimental information concerning α_1 and α_2 has been given recently by Dalgarno.[11] The value of β_1 for H was given by Mittleman. An estimate of β_1 for He has also been obtained.[12]

The Mittleman-Watson derivation is very similar to a derivation presented in Appendix A based on a study of the equivalent one-body problem in Feshbach's[13] formulation in which the projection operator P projects on to the unperturbed target ground state. A more natural choice of projection operator would seem to be that associated with the adiabatic approximation; for each value of $\mathbf{q}$, one projects on to the ground state of the target in the presence of the potential generated by the incident particle fixed at $\mathbf{q}$. The adiabatic approach has the advantage that the adiabatic $1/q^4$ term is thereby atuomatically accounted for, as is the adiabatic component of the $1/q^6$ term. The role of the perturbation operator is then largely played by the kinetic energy operator $T(\mathbf{q})$ of the incident particle rather than by the interaction of the incident particle with the target particles. We have not actually obtained the next term in the long-range potential—the term which goes as $1/q^7$—but we believe that is thould be easier to obtain using the adiabatic ground-state wave-function approach than the unperturbed ground-state wave-function approach. Apart from the question of the choice of the projection operator, our results represent a useful though formally trivial extension of those of Mittleman and Watson[9,10] in that they are applicable to any atom or ion for which the scattering problem can be reduced to an analysis of one or more single-channel scattering processes; this includes atoms whose ground states can, in a sensible approximation, be said to have orbital angular momenta $L=0$. (An extension to multichannel problems should present no real difficulties.)

Since we are not attempting an approach from first principles, it will be useful to consider the possibility of determining α_1, α_2, and β_1 experimentally, by means *other* than an analysis of experimental scattering data. More generally, it will be interesting to consider how far one can go in an attempt to determine scattering parameters such as phase shifts and cross sections without doing scattering experiments.

The determination of the parameters which characterize a modified effective-range theory expansion can be viewed as an optical-model potential approach (with the long-range behavior built in) which has been so helpful in nuclear physics and whose potentialities in atomic physics have been considered by a number of people and stressed by Gerjuoy.[14]

2. FORMULATION IN TERMS OF ADIABATIC STATES

We consider the single-channel (elastic) scattering of particles of positive or negative charge e' by spherically symmetric atoms or ions which contain z electrons and a nucleus of infinite mass and charge Ze. We take the incident particle to be distinguishable from the target electrons. For present purposes, this does *not* exclude incident electrons, for we are interested in the long-range behavior of the effective interaction, and an electron at great distances from the target is distinguishable from the target electrons. (The argument is not completely convincing, especially since the slowly moving incident particle has a long wavelength. Some more formal if still not rigorous arguments to justify an approach in which the Pauli principle is not used have been presented.[3] We shall assume that such an approach is

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justified.) The total Hamiltonian H is then given by

$$H(\mathbf{r},\mathbf{q})=H_T(\mathbf{r})+T(\mathbf{q})+V(\mathbf{r},\mathbf{q}), \tag{2.1}$$

where H_T is the target Hamiltonian with $\mathbf{r}$ denoting the space and spin variables of all the electrons, $T(\mathbf{q})$ is the kinetic-energy operator of the incoming particle with a mass which is to be negligible relative to that of the target, and $V(\mathbf{r},\mathbf{q})$ is the interaction potential between the incident particle and the target particles, which we assume to be spin-independent. It will be convenient to break up $V(\mathbf{r},\mathbf{q})$ into its unshielded and shielded components,

$$V(\mathbf{r},\mathbf{q})=V_{\text{unsh}}(q)+V_{\text{sh}}(\mathbf{r},\mathbf{q}), \tag{2.2}$$

where

$$V_{\text{unsh}}(q)=(Z-z)ee'/q$$

and

$$V_{\text{sh}}(\mathbf{r},\mathbf{q})=ee'\left[\frac{z}{q}-\sum_{i=1}^{z}\frac{1}{|\mathbf{r}_i-\mathbf{q}|}\right]. \tag{2.3}$$

The total energy of the system is

$$E=E_{T0}+E',$$

where E' is the initial kinetic energy of the projectile and E_{T0} is the ground-state energy of the target. The orthonormal target eigenfunctions $\psi_{Tn}(\mathbf{r})$ defined by

$$H_T(\mathbf{r})\psi_{Tn}(\mathbf{r})=E_{Tn}\psi_{Tn}(\mathbf{r}) \tag{2.4}$$

are completely antisymmetrized with respect to exchanges of target electrons.

For E' relatively small compared to the first excitation energy, $E_{T1}-E_{T0}$, the states ψ_{Tn} will often be very much distorted adiabatically by the interaction V. It therefore seems useful to expand not in terms of the $\psi_{Tn}(\mathbf{r})$, which are generated by $H_T(\mathbf{r})$, but in terms of the orthonormal set of functions $\phi_n(\mathbf{r},\mathbf{q})$ with associated energy eigenvalues $\mathcal{E}_n(q)$ generated by $H_T(\mathbf{r})+V_{\text{sh}}(\mathbf{r},\mathbf{q})$. We have

$$[H_T(\mathbf{r})+V_{\text{sh}}(\mathbf{r},\mathbf{q})-\mathcal{E}_n(q)]\phi_n(\mathbf{r},\mathbf{q})=0, \tag{2.5}$$

where, for each fixed value of $\mathbf{q}$,

$$\int\phi_n(\mathbf{r},\mathbf{q})\phi_m(\mathbf{r},\mathbf{q})d\mathbf{r}=\delta_{nm}. \tag{2.6}$$

The ϕ_n will be taken to be real, as will all wave functions throughout the paper. The ϕ_n are to be regular at the origin and are to behave asymptotically as

$$\phi_n(\mathbf{r},\mathbf{q})\to\psi_{Tn}(\mathbf{r}),\quad q\to\infty.$$

(For special cases, such as the H atom and hydrogen-like ions, there are special problems associated with degeneracy, but these can easily be handled.) We introduce the potentials $v_n(q)$ defined by

$$v_n(q)\equiv\mathcal{E}_n(q)-E_{Tn}. \tag{2.7}$$

We then have

$$v_n(q)\to 0,\quad q\to\infty,$$

since $\mathcal{E}_n(q)$ approaches E_{Tn} asymptotically.

We now introduce the adiabatic projection operator P_a defined for each value of $\mathbf{q}$ by

$$P_a\equiv\phi_0\rangle\langle\phi_0. \tag{2.8}$$

Explicitly, for an arbitrary function $f(\mathbf{r},\mathbf{q})$, we have, for each value of $\mathbf{q}$,

$$P_af(\mathbf{r},\mathbf{q})=\phi_0(\mathbf{r},\mathbf{q})\int\phi_0(\mathbf{r}',\mathbf{q})f(\mathbf{r}',\mathbf{q})d\mathbf{r}'.$$

With the adiabatic excited-state projection operator Q_a defined by

$$Q_a\equiv 1-P_a,$$

we have

$$P_a^2=P_a,\quad Q_a^2=Q_a,\quad\text{and}\quad P_aQ_a=Q_aP_a=0.$$

The original Schrödinger equation

$$(H-E)\Psi=0$$

can be rewritten as a set of coupled equations for the components $P_a\Psi$ and $Q_a\Psi$ rather than in terms of the components $P\Psi$ and $Q\Psi$. We then have

$$P_a(H-E)P_a\Psi=-P_aHQ_a\Psi,$$
$$Q_a(H-E)Q_a\Psi=-Q_aHP_a\Psi.$$

They can be formally uncoupled as

$$P_a[H+HG^{Q_a}H-E]P_a\Psi=0, \tag{2.9}$$

$$Q_a[H+HG^{P_a}H-E]Q_a\Psi=-Q_aHP_a\Psi^{P_a}, \tag{2.10}$$

where G^{P_a}, G^{Q_a}, and $P_a\Psi^{P_a}$ are defined by

$$P_a(H-E)P_aG^{P_a}=-P_a, \tag{2.11}$$

$$Q_a(H-E)Q_aG^{Q_a}=-Q_a, \tag{2.12}$$

$$P_a(H-E)P_a\Psi^{P_a}=0, \tag{2.13}$$

and by appropriate boundary conditions.

The equivalent one-body equation (2.9) contains all of the scattering information contained in the original Schrödinger equation. We will now rewrite this equation in a form in which the effective interaction is exhibited explicitly. To begin, we define the adiabatic one-body function $u_{0a}(\mathbf{q})$ by

$$u_{0a}(\mathbf{q})\equiv\int\phi_0(\mathbf{r}',\mathbf{q})\Psi(\mathbf{r}',\mathbf{q})d\mathbf{r}'. \tag{2.14}$$

We then have

$$P_a\Psi\equiv\phi_0(\mathbf{r},\mathbf{q})u_{0a}(\mathbf{q}). \tag{2.15}$$

Using Eqs. (2.1), (2.2), (2.5), and (2.15), we can write

$$P_aHP_a\Psi=\phi_0(\mathbf{r},\mathbf{q})\Big\{T(\mathbf{q})+V_{\text{unsh}}(q)+\mathcal{E}_0(q)+\int\phi_0(\mathbf{r},\mathbf{q})[T(\mathbf{q})\phi_0(\mathbf{r},\mathbf{q})]d\mathbf{r}\Big\}u_{0a}(\mathbf{q}), \tag{2.16}$$

where the square bracket indicates that the $T(\mathbf{q})$ within the square bracket is to operate on $\phi_0(\mathbf{r},\mathbf{q})$ only. In arriving at (2.16), we used the fact that the cross term arising from the application of $T(\mathbf{q})$ vanishes, that is,

$$2\int \phi_0(\mathbf{r},\mathbf{q})[\nabla_q\phi_0(\mathbf{r},\mathbf{q})]d\mathbf{r}\cdot\nabla_q u_{0a}(\mathbf{q}) = [\nabla_q u_{0a}(\mathbf{q})]\cdot\nabla_q\int\phi_0^2(\mathbf{r},\mathbf{q})d\mathbf{r}=0,$$

since

$$\int\phi_0^2 d\mathbf{r}=1.$$

We next consider the term in (2.9) involving G^{Q_a}. From the definition of ϕ_0, (2.5), and of P_a, (2.8), it follows that

$$P_aHQ_a=P_aTQ_a \quad\text{and}\quad Q_aHP_a=Q_aTP_a.$$

Dropping a factor of $\phi_0\rangle$ on the left, we can now rewrite (2.9) as

$$[T(\mathbf{q})+\mathcal{U}-E']u_{0a}(\mathbf{q})=0, \tag{2.17}$$

with

$$\mathcal{U}=V_{\text{unsh}}(q)+v_0(q)+v_0', \tag{2.18}$$

where $v_0(q)$, defined by (2.7), is the additional energy of the system due to the adiabatic interaction of various multipoles of the ground state of the target with the incident particle fixed at $\mathbf{q}$ and where the nonlocal operator v_0' is defined by

$$v_0'u_{0a}(\mathbf{q})\equiv\int\phi_0(\mathbf{r},\mathbf{q})[T(\mathbf{q})\phi_0(\mathbf{r},\mathbf{q})]d\mathbf{r}\times u_{0a}(\mathbf{q})+v_0''u_{0a}(\mathbf{q}), \tag{2.19}$$

where the operator v_0'' is defined by

$$v_0''u_{0a}(\mathbf{q})\equiv\int\phi_0(\mathbf{r},\mathbf{q})T(\mathbf{q})G^{Q_a}(\mathbf{r},\mathbf{q};\mathbf{r}',\mathbf{q}')T(\mathbf{q}')\phi_0(\mathbf{r}',\mathbf{q}')\times u_{0a}(\mathbf{q}')d\mathbf{r}d\mathbf{r}'d\mathbf{q}'. \tag{2.20}$$

Note the explicit appearance of $T(\mathbf{q})$ in each term in $v_0'(q)$. Equations (2.19) and (2.20) will provide the basis for our discussion in the next section, where v_0 and v_0' will be studied asymptotically using perturbation theory. It is often possible to evaluate the asymptotic form of ϕ_0 rather accurately. One can then obtain v_0 and the first term of v_0' rather accurately. On the other hand, the appearance of G^{Q_a} means that the second term in v_0' is a highly complicated nonlocal interaction which is very difficult to treat accurately even asymptotically. It will be shown, however, that the term in G^{Q_a} only contributes terms of order $1/q^8$.

3. LONG-RANGE BEHAVIOR OF THE EFFECTIVE POTENTIAL

The definition in Sec. 2 of the equivalent one-body potential $\mathcal{U}$ is valid, apart from the question of antisymmetrization, for all values of q. To be useful for all values of q we must determine $\phi_0(\mathbf{r},\mathbf{q})$ and G^{Q_a}, but the problem of determining G^{Q_a} is generally more difficult than that of solving the original Schrödinger equation. The approach of Sec. 2 is, however, a very useful one if we limit ourselves to a determination of the long-range behavior of $\mathcal{U}$, or, more precisely, to terms in $1/q^7$, for the term in G^{Q_a} does not then contribute at all and ϕ_0 need only be determined asymptotically. To perform this determination, we first obtain the integral equation satisfied by ϕ_0.

ϕ_0 satisfies (2.5), which we rewrite as

$$[H_T(\mathbf{r})-E_{T0}]\phi_0(\mathbf{r},\mathbf{q}) = -[V_{\text{sh}}(\mathbf{r},\mathbf{q})-v_0(q)]\phi_0(\mathbf{r},\mathbf{q}), \tag{3.1}$$

is regular at the origin, and approaches $\psi_{T0}(\mathbf{r})$ as $q\to\infty$. The normalization of ϕ_0 is given by Eq. (2.6). We introduce the Green's function $g_0(\mathbf{r},\mathbf{r}')$ associated with the target; g_0 is to satisfy

$$[H_T(\mathbf{r})-E_{T0}]g_0(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}'), \tag{3.2}$$

is to be symmetric in $\mathbf{r}$ and $\mathbf{r}'$, is to be regular at the origin, and is to vanish asymptotically. Since $\psi_{T0}(\mathbf{r})$ is a solution of the homogeneous equation obtained from (3.2) by dropping the delta function, g_0 is defined uniquely only to within the additive term $c\psi_{T0}(\mathbf{r})\psi_{T0}(\mathbf{r}')$, where c is an arbitrary constant. It will be convenient to choose g_0 to be orthogonal to $\psi_{T0}(\mathbf{r})$ [and therefore to $\psi_{T0}(\mathbf{r}')$]. We can then invert (3.1) and write

$$\phi_0(\mathbf{r},\mathbf{q})=N(q)\psi_{T0}(\mathbf{r}) + \int g_0(\mathbf{r},\mathbf{r}')[V_{\text{sh}}(\mathbf{r}',\mathbf{q})-v_0(q)]\phi_0(\mathbf{r}',\mathbf{q})d\mathbf{r}'. \tag{3.3}$$

$N(q)$ is determined to within a phase factor by the normalization condition satisfied for each value of $\mathbf{q}$ by ϕ_0.

Finally, we let q be large. For sufficiently large q, we can be sure that the solution of (3.3) obtained by iteration converges. We then have

$$\phi_0(\mathbf{r},\mathbf{q})=N(q)\Big\{\psi_{T0}(\mathbf{r})+\int g_0(\mathbf{r},\mathbf{r}')V_{\text{sh}}(\mathbf{r}',\mathbf{q})\psi_{T0}(\mathbf{r}')d\mathbf{r}' + \int g_0(\mathbf{r},\mathbf{r}')[V_{\text{sh}}(\mathbf{r}',\mathbf{q})-v_0(q)]g_0(\mathbf{r}',\mathbf{r}'')\times V_{\text{sh}}(\mathbf{r}'',\mathbf{q})\psi_{T0}(\mathbf{r}')d\mathbf{r}'d\mathbf{r}''+\cdots\Big\}, \tag{3.4}$$

where the orthogonality of g_0 to ψ_{T0} accounts for the omission of terms containing $v_0(q)$ on a number of occasions. The number of terms in (3.4) that must be retained depends upon how far in powers of $1/q$ one wishes to obtain the equivalent one-body potential.

Since we are considering large values of q, we can replace (2.3) by

$$V_{\rm sh}(\mathbf{r},\mathbf{q}) \to -ee' \sum_{l=1}^{\infty} \frac{J_l(\mathbf{r},\hat{q})}{q^{l+1}} \quad \text{as} \quad q \to \infty\,, \tag{3.5}$$

where

$$J_l(\mathbf{r},\hat{q}) \equiv \sum_{i=1}^{z} r_i{}^l P_l(\cos\theta_i)\,, \tag{3.6}$$

with θ_i the angle between $\mathbf{r}_i$ and $\mathbf{q}$. Since $v_0(q)$ behaves asymptotically as $1/q^4$, we can rewrite (3.4) as

$$\phi_0(\mathbf{r},\mathbf{q}) = N(q)\left\{\psi_{T0}(\mathbf{r}) - ee' \sum_{l=1}^{z} \frac{1}{q^{l+1}} \int g_0 J_l \psi_{T0} d\mathbf{r}' + \frac{(ee')^2}{q^4} \int g_0 J_1 g_0 J_1 \psi_{T0} d\mathbf{r}' d\mathbf{r}'' + O\left(\frac{1}{q^5}\right)\right\}. \tag{3.7}$$

It is convenient to introduce the functions χ_l defined by

$$\chi_l(\mathbf{r},\hat{q}) \equiv e^2 \int g_0(\mathbf{r},\mathbf{r}') J_l(\mathbf{r}',\hat{q}) \psi_{T0}(\mathbf{r}') d\mathbf{r}'\,. \tag{3.8}$$

The χ_l then satisfy

$$[H_T(\mathbf{r}) - E_{T0}]\chi_l(\mathbf{r},\hat{q}) = -e^2 J_l(\mathbf{r},\hat{q})\psi_{T0}(\mathbf{r})\,. \tag{3.9}$$

Since $g_0(\mathbf{r},\mathbf{r}')$ is orthogonal to $\psi_{T0}(\mathbf{r})$, it follows from (3.8) that

$$\int \psi_{T0}(\mathbf{r})\chi_l(\mathbf{r},\hat{q}) d\mathbf{r} = 0\,. \tag{3.10}$$

Equation (3.7) can now be rewritten as

$$\phi_0(\mathbf{r},\mathbf{q}) = N(q)\left\{\psi_{T0}(\mathbf{r}) - \frac{e'}{e} \sum_{l=1}^{z} \frac{\chi_l(\mathbf{r},\hat{q})}{q^{l+1}} + \frac{(e')^2}{q^4} \int g_0 J_1 \chi_1 d\mathbf{r}' + O\left(\frac{1}{q^5}\right)\right\}. \tag{3.11}$$

Using the orthonormality condition (2.6) and the orthogonality of ψ_{T0} to g_0 and to χ_l, and introducing the set of numbers

$$\beta_l \equiv \int \chi_l{}^2(\mathbf{r},\hat{q}) d\mathbf{r}\,, \tag{3.12}$$

we find

$$1 = N^2(q)\left\{1 + \left(\frac{e'}{e}\right)^2 \frac{\beta_1}{q^4} + O\left(\frac{1}{q^5}\right)\right\},$$

or, with a particular choice of phase,

$$N(q) = 1 - \left(\frac{e'}{e}\right)^2 \frac{\beta_1}{2q^4} + O\left(\frac{1}{q^5}\right). \tag{3.13}$$

We have finally

$$\phi_0(\mathbf{r},\mathbf{q}) = \left[1 - \left(\frac{e'}{e}\right)^2 \frac{\beta_1}{2q^4}\right]\psi_{T0}(\mathbf{r}) - \frac{e'}{e} \sum_{l=1}^{z} \frac{\chi_l(\mathbf{r},\hat{q})}{q^{l+1}} + \frac{(e')^2}{q^4} \int g_0 J_1 \chi_1 d\mathbf{r}' + O\left(\frac{1}{q^5}\right) F(\mathbf{r},\hat{q})\,. \tag{3.14}$$

The precise form of the function $F(\mathbf{r},\hat{q})$ is not needed for present purposes. The expansion (3.14) is the polarized orbital wave function obtained previously by a number of authors.[15,16]

We are now in a position to determine the long-range behavior of v. To obtain $v_0(q)$, we multiply Eq. (3.1) on the left by $\psi_{T0}(\mathbf{r})$, integrate over $d\mathbf{r}$, use Eq. (2.4), and arrive at

$$v_0(q) \int \psi_{T0}(\mathbf{r})\phi_0(\mathbf{r},\mathbf{q}) d\mathbf{r} = \int \psi_{T0}(\mathbf{r}) \times V_{\rm sh}(\mathbf{r},\mathbf{q})\phi_0(\mathbf{r},\mathbf{q}) d\mathbf{r}\,. \tag{3.15}$$

Inserting ϕ_0 as given by (3.14) and using the orthogonality of ψ_{T0} to χ_l and to g_0, the left-hand side of (3.15) becomes

$$\text{l.h.s.} = v_0(q)\left[1 - \left(\frac{e'}{e}\right)^2 \times \frac{\beta_1}{2q^4} + O\left(\frac{1}{q^5}\right)\right].$$

Inserting ϕ_0 as given by (3.14) into the right-hand side of (3.15), we arrive at

$$\text{r.h.s.} = R_1(q) + R_2(q) + R_3(q) + R_4(q)\,,$$

where

$$R_1(q) = \left[1 - \left(\frac{e'}{e}\right)^2 \times \frac{\beta_1}{2q^4}\right] \int \psi_{T0}{}^2(\mathbf{r}) V_{\rm sh}(\mathbf{r},\mathbf{q}) d\mathbf{r}\,,$$

$$R_2(q) = -\frac{e'}{e} \sum_{l=1}^{z} \frac{1}{q^{l+1}} \int \psi_{T0}(\mathbf{r}) V_{\rm sh}(\mathbf{r},\mathbf{q}) \chi_l(\mathbf{r},\hat{q}) d\mathbf{r}\,,$$

$$R_3(q) = \frac{(e')^2}{q^4} \int \psi_{T0}(\mathbf{r}) V_{\rm sh}(\mathbf{r},\mathbf{q}) g_0(\mathbf{r},\mathbf{r}') J_1(\mathbf{r}',\hat{q}) \chi_1(\mathbf{r}',\hat{q}) d\mathbf{r} d\mathbf{r}'\,,$$

$$R_4(q) = O\left(\frac{1}{q^5}\right) \times \int \psi_{T0}(\mathbf{r}) V_{\rm sh}(\mathbf{r},\mathbf{q}) F(\mathbf{r},\hat{q}) d\mathbf{r}\,.$$

The integral in $R_1(q)$ vanishes exponentially with q by virtue of the assumed $L=0$ property of the ground state. $R_3(q)$ vanishes as q^{-7} since $J_1(\mathbf{r}',\hat{q})$ and $\chi_1(\mathbf{r}',\hat{q})$ combine

[15] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); C. Schwartz, Ann. Phys. (N. Y.) **6**, 170 (1959); A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961); A. Dalgarno, in *Perturbation Theory and its Applications in Quantum Mechanics*, edited by C. H. Wilcox (John Wiley & Sons, Inc., New York, 1966), p. 145.

[16] In the first preliminary report referred to at the very beginning of the paper, it was stated that for a charged particle incident on an ion, there was a $1/q^6$ term, but this is not so.

to give a function which transforms like $L=0$ or $L=2$ so that one must choose the $L=2$ component of V_{sh}, a component which goes as $1/q^3$. $R_4(q)$ vanishes at least as $1/q^7$ since V_{sh} goes at least as $1/q^2$. Introducing the electric multipole polarizabilities α_l numbers defined by

$$\alpha_l \equiv -2(\psi_{T0}, J_l \chi_l) = -2e^2(\psi_{T0}, J_l g_0 J_l \psi_{T0}), \quad (3.16)$$

and noticing that $(\psi_{T0}, J_l \chi_{l'})=0$ for $l \neq l'$, we have, using Eq. (3.5),

$$R_2(q) = -\tfrac{1}{2}(e')^2\left[\frac{\alpha_1}{q^4}+\frac{\alpha_2}{q^6}+O\left(\frac{1}{q^8}\right)\right].$$

Equating the left- and right-hand sides, we find

$$v_0(q) = -\tfrac{1}{2}(e')^2\left[\frac{\alpha_1}{q^4}+\frac{\alpha_2}{q^6}+O\left(\frac{1}{q^7}\right)\right]. \quad (3.17)$$

We turn our attention now to the determination of v_0' as given by (2.19). To evaluate the first term, we operate on (3.14) with $T(\mathbf{q})$ and obtain

$$[T(\mathbf{q})\phi_0(\mathbf{r},\mathbf{q})] \rightarrow -(e'/e)^2 \times \tfrac{1}{2}\beta_1 \psi_{T0}(\mathbf{r})[Tq^{-4}] + (e')^2 \int g_0 J_1 \chi_1 d\mathbf{r}'[Tq^{-4}] + O(q^{-7}). \quad (3.18)$$

In arriving at this result, we used the relationship

$$T(q)\sum_l \frac{P_l(\cos\theta_i)}{q^{l+1}} = 0, \quad (3.19)$$

valid since we are not concerned with $q=0$, and we used the fact that

$$\int g_0(\mathbf{r},\mathbf{r}') J_1(\mathbf{r}',\hat{q}) \chi_1(\mathbf{r}',\hat{q}) d\mathbf{r}'$$

is independent of $\hat{q}$. Multiplying (3.18) by ϕ_0 on the left and integrating over $\mathbf{r}$, we use the orthogonality of ψ_{T0} and g_0 to arrive at

$$\int \phi_0(\mathbf{r},\mathbf{q}) T(\mathbf{q}) \phi_0(\mathbf{r},\mathbf{q}) d\mathbf{r} = \left(\frac{e'}{e}\right)^2 \tfrac{1}{2}\beta_1 \frac{\hbar^2}{2m}\frac{4\times 3}{q^6} + O\left(\frac{1}{q^7}\right). \quad (3.20)$$

The proof that v_0'', defined by Eq. (2.20), contributes asymptotically only as $1/q^8$ is indicated in Appendix B.

From Eqs. (2.18), (3.17), and (3.20), we find that to order $1/q^6$, $\mathcal{U}$ is local and energy-independent, being given by Eq. (1.1), where the α_l and β_l are defined by Eqs. (3.16) and (3.12), respectively. [Since α_l and β_l are proportional to e^2 and to e^4, respectively, it follows that $\mathcal{U}$ as given by (1.1) depends, as it must, only on the product ee'.]

4. DOMAIN OF VALIDITY OF THE EXPANSION

The expansion of $\mathcal{U}(q)$ in powers of $1/q$, as given by (1.1), is valid "for sufficiently large q," or, more precisely, for q sufficiently large for the iteration of ϕ_0 given in (3.4) to converge. That the iteration will converge for q large enough, say, $q>\bar{q}$, is reasonably clear on physical grounds. The contribution to the phase shift of those terms with an energy dependence less than that associated with short-range potentials, namely, k^{2L+1}, will be completely determined by (1.1), *independent of the value of* $\bar{q}$, "for sufficiently small energies." If, however, $\bar{q}$ is very large, those terms in the expression for the phase shift which have their origin in short-range potentials will have such large coefficients that even though they behave as k^{2L+1} or some higher power of k, the energy domain validity of the terms arising from (1.1) alone, some of which go as k^2, for example, will only be from zero energy up to some infinitesimal energy.

In other words, we are faced with the fact that in actual practice one really wants to have some idea of the range of q for which the expansion (3.14) for ϕ_0 is valid and for which, therefore, the expansion (1.1) for $\mathcal{U}$ is valid. Put slightly differently, one wants to know where to cut off or alter $\mathcal{U}$ as q varies from $q=\infty$ to smaller values of q. This question will not normally be answerable from first principles. A more complete discussion will be given elsewhere.[8] Here, we simply comment that one could attempt, as one of many possibilities, to replace q^{-4} by $(q^4+a)^{-1}$ and q^{-6} by $(q^6+b)^{-1}$, in (1.1), for *all* values of q, with a and b constants to be determined empirically which presumably parametrize short-range effects due to exchange, the excitation of higher states, etc. Note that the usual replacement of q^{-4} by $(q^2+d^2)^2$ would not be consistent in the present context for it has contributions which go as q^{-6} as well as q^{-4} and we have here determined the correct coefficient of q^{-6}. In any reasonably refined treatment, it might be necessary to take a and b to be functions of L.

5. EVALUATION OF β_1

We now turn our attention to the question of obtaining numerical values for β_1 for various atoms.

A. H-Like Systems

For H and H-like systems, χ_1 is known exactly,[15] and Eq. (3.11) leads immediately to

$$\beta_1(Z, \text{H-like system}) = (43/8)(a_0^4/Z^6). \quad (5.1)$$

(It is clear that β_1 for H-like systems must go as Z^{-6} since it is proportional to the square of a length and inversely proportional to the square of an energy.) For $Z=1$, Eq. (5.1) reduces to the value obtained previously.[10]

B. Direct Use of Approximations to χ_1

For other than the one-electron case, the method that would probably yield the most reliable results for most systems would be to use χ_1 as obtained from Eq. (3.8), an equation especially suited for the numerical evaluation of χ_1. Reasonably accurate approximations to χ_1 have been obtained by Sternheimer[15] and others for many different atoms. We will restrict ourselves to the case of He, for which a relatively simple analytic approximation to χ_1 was obtained by Schwartz.[15] This leads to the estimate $\beta_1(\mathrm{He})=0.46a_0^4$, an estimate which can not be expected to be very accurate since the use in Eq. (3.12) of the same approximation to χ_1 leads to an estimate of α_1 which is 20% lower than the best estimates available. A value of $0.44a_0^4$ has been obtained by LaBahn and Callaway[12] using a somewhat more complicated approximation to χ_1. Statistical moment studies lead to a presumably better estimate of $\beta_1(\mathrm{He})$. (See end of Sec. 5.)

C. Dipole-Oscillator Strengths

We turn now to a second method of obtaining β_1, in which β_1 is expressed in terms of the electric dipole oscillator strengths, the dipole transition matrix elements from the ground state ψ_{T0} defined by

$$f_{0n}=\frac{2m(E_{Tn}-E_{T0})}{3e^2\hbar^2}|(\psi_{T0},\mathfrak{y}_1\psi_{Tn})|^2, \tag{5.2}$$

where

$$\mathfrak{y}_1\equiv -e\sum_i \mathbf{r}_i.$$

It is well known from studies of α_1, which can also be expressed in terms of the f_{0n}, that the use of the f_{0n} does not lead to very accurate estimates, both because the f_{0n} for n representing a bound state are normally not known very accurately and because the method does not readily allow one to take into account contributions from the continuum. Nevertheless, the use of the f_{0n} allows quick if rough estimates and will provide us with some orientation. Further, the estimates provided by the use of the f_{0n} should be somewhat more reliable for β_1 than for α_1. This follows from the fact, to be shown, that the expression for β_1 contains one more energy denominator than the expression for α_1, thereby reducing the relative contributions from the higher energy states and in particular from the continuum states whose contributions we are here neglecting. (It will also be possible to partially account for the continuum contribution if α_1 is known experimentally.)

To express β_1 in terms of the f_{0n}, we begin by noting that it follows from the equation which defines it, Eq. (3.2), that g_0 can be written as

$$g_0(\mathbf{r},\mathbf{r}')=\sum{}'\psi_{Tn}(\mathbf{r})\rangle\langle\psi_{Tn}(\mathbf{r}')/(E_{T0}-E_{Tn}), \tag{5.3}$$

where the prime denotes the exclusion of $n=0$, the ground state. It follows directly from Eq. (3.8) that

$$\chi_l=e^2\sum_n{}'\psi_{Tn}(\psi_{Tn},J_l\psi_{T0})/(E_{T0}-E_{Tn}). \tag{5.4}$$

We immediately obtain, from (3.12),

$$\beta_l=e^4\sum_n{}'|(\psi_{Tn},J_l\psi_{T0})|^2/(E_{T0}-E_{Tn})^2. \tag{5.5}$$

In particular, we have

$$\beta_1=e^4\sum_n{}'|(\psi_{Tn},\sum_{i=1}^{z}r_i\cos\theta_i\psi_{T0})|^2/(E_{T0}-E_{Tn})^2, \tag{5.6}$$

where we used Eq. (3.6). Because of the equality of the x, y, and z component contributions, we can rewrite Eq. (5.6) as

$$\beta_1=\frac{e^2}{3}\sum_n{}'|(\psi_{Tn},\mathfrak{y}_1\psi_{T0})|^2/(E_{T0}-E_{Tn})^2.$$

We can now express β_1 in terms of the oscillator strengths as

$$\beta_1=\frac{e^4\hbar^2}{2m}\sum_n{}'f_{0n}/(E_{Tn}-E_{T0})^3. \tag{5.7}$$

If we use Eq. (5.4) in Eq. (3.16), we obtain the standard relation

$$\alpha_l=2e^2\sum_n{}'|(\psi_{T0},J_l\psi_{Tn})|^2/(E_{Tn}-E_{T0}). \tag{5.8}$$

In particular, we have

$$\alpha_1=\tfrac{2}{3}\sum_n{}'|(\psi_{T0},\mathfrak{y}_1\psi_{Tn})|^2/(E_{Tn}-E_{T0})$$
$$=(e^2\hbar^2/m)\sum_n{}'f_{0n}/(E_{Tn}-E_{T0})^2. \tag{5.9}$$

Since each of the terms in Eq. (5.7) is positive, a lower bound on β_1 is obtained by utilizing the experimentally or theoretically known values of f_{0n} and E_{Tn} for the first N contributions, that is, we have the lower bound

$$\beta_1\geq\beta_{1L}(N)\equiv\frac{e^4\hbar^2}{2m}\sum_{n=1}^{N}f_{0n}/(E_{Tn}-E_{T0})^3. \tag{5.10}$$

To obtain an upper bound on β_1, we introduce $\alpha_1(N)$ defined by

$$\alpha_1(N)\equiv\frac{e^2\hbar^2}{m}\sum_{n=1}^{N}f_{0n}/(E_{Tn}-E_{T0})^2.$$

With a slight generalization of a technique which was used in the earliest calculations of α_1, we then have, since

$$(E_{Tn}-E_{T0})^{-3}\leq(E_{T,N+1}-E_{T0})^{-1}(E_{Tn}-E_{T0})^{-2} \quad \text{for} \quad n\geq N+1,$$

that

$$\beta_1\leq\beta_{1U}(N)\equiv\beta_{1L}(N)+\tfrac{1}{2}e^2(E_{T,N+1}-E_{T0})^{-1}[\alpha_1-\alpha_1(N)]. \tag{5.11}$$

TABLE I. A lower bound $\beta_{1L}(N)$ [see Eq. (5.10)] and an upper bound $\beta_{1U}(N)$ [see Eq. (5.11)] on β_1. β_1 is a measure of the nonadiabatic contribution to the $1/q^6$ term in the interaction. The dipole oscillator strengths f_{0n} and the excitation energies of the first $N+1$ excited states are used, as is the value of the electric dipole polarizability α_1. N is the number of terms used in (5.10) and (5.11).

Atom	N	$\beta_{1L}(N)/a_0^4$	$\beta_{1U}(N)/a_0^4$	Uncertainties in f_{0n} (%)
H[a]	40	4.7	5.6	1
He[a]	11	0.4	0.8	1–10
Li[a]	12	1200	1205	1–10
Ne[a]	2	0.03	2.2	25
Na[b]	16	735	745	10–25

[a] The values for $E_{Tn}-E_{T0}$ and f_{0n}, and the characteristic uncertainties in the latter, were obtained from W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities, Hydrogen Through Neon* (U. S. Government Printing Office, Washington, D. C., 1966), Vol. I.
[b] M. W. Smith (private communication); see also V. K. Prokofjew, Z. Physik **58**, 225 (1929).

The utilization of this inequality requires a knowledge of α_1, of f_{0n} for $n=1$ to N, and of $E_{Tn}-E_{T0}$ for $n=1$ to $N+1$. Some results obtained from Eqs. (5.10) and (5.11) are listed in Table I.

The difference between the upper and lower bounds is a measure of the error introduced by the use of a restricted set of f_{0n}. An *additional* error is introduced due to the uncertainty in the values of the f_{0n}. Some characteristic estimates of these latter uncertainties are listed in column 5. A more realistic determination of lower and upper bounds could be obtained by reducing the lower bound estimate [column (3)] and increasing the upper bound estimate [column (4)] by the estimated percentage error of the f_{0n}.

D. Variational Bounds

We now consider the possibility of obtaining an estimate of β_1 which is a variational bound. To begin, we note that, *assuming* ψ_{T0} to be known, variational bounds on α_l are well known. This is to be expected, since an atom in a very weak uniform electric field $\mathcal{E}$ has an energy $E=-\frac{1}{2}\alpha_1\mathcal{E}^2+E_{T0}$. A variational upper bound on E can be obtained by a Rayleigh-Ritz calculation, and if E_{T0} can be extracted, which is possible if ψ_{T0} is known, a variational lower bound on α_1 follows. A similar statement is valid for α_l for any l on restricting the correction to ψ_{T0} in the trial function to states of angular momentum l. A neater way of obtaining a variational lower bound on α_l is as follows. From Eq. (3.16), we have

$$\alpha_l=2e^2(\psi_{T0},J_l[-g_0]J_l\psi_{T0}), \tag{5.12}$$

where

$$-g_0=-G_0^Q=\frac{1}{Q(H_T-E_{T0})Q}$$

is a positive-definite operator and can therefore be bounded by[17]

$$-g_0\geq\frac{F\rangle\langle F}{(F,Q[H_T-E_{T0}]QF)}, \tag{5.13}$$

where F is an arbitrary function in Q space. The insertion of Eq. (5.13) into Eq. (5.12) reproduces the variational lower bound on α_l.

We know of no simple physical static interpretation of β_1 and it is not immediately clear therefore, since the Rayleigh-Ritz approach is not applicable, that one can obtain a variational bound on β_1. It is, however, trivial to obtain such a bound, assuming again that ψ_{T0} is known, though the bound is a much more difficult one to use than the bound on α_1. Thus, rewriting Eq. (5.6) as

$$\beta_1=e^4(\psi_{T0},J_1g_0^2J_1\psi_{T0}), \tag{5.14}$$

we have, since g_0^2 is a positive-definite operator,

$$g_0^2\geq\frac{F\rangle\langle F}{(F,[Q(H_T-E_{T0})Q]^2F)}. \tag{5.15}$$

The insertion of inequality (5.15) into Eq. (5.14) provides us with a variational lower bound on β_1, but the denominator of (5.15) is a very complicated quantity to calculate for any moderately realistic approximation F to $g_0\chi$. [It may be worth recording that the statement that $A>B>0$ for A and B Hermitian operators does *not* unfortunately imply that $A^2>B^2$; were this true, one could immediately obtain a simple variational lower bound on β_1 by squaring inequality (5.13).]

It is interesting to note that the usual Born-Oppenheimer (BO) approximation results when the v_0' term in $\mathcal{V}$ is dropped. Since Eqs. (2.17) and (2.18) represent an exact statement of the problem, we may be in a position to make more precise judgments about the validity of the BO approximation. Thus, it has been shown,[18] for single-channel elastic scattering of a particle by a target of infinite mass, that v_0' can often be proven to be nonnegative. For such a case, the solution of Eq. (2.17), with v_0' neglected, gives an upper bound (the adiabatic approximation) on the phase shift. It is also sometimes possible to show that the exceedingly difficult v_0'' term defined by Eq. (2.20) is nonpositive. It follows that the phase shift defined by $V_{\text{unsh}}+v_0$ plus the first potential of v_0' in Eq. (2.19) generates a lower bound on the phase shift.

E. Statistical Moments

Estimates of and bounds on β_1 and more generally on the β_l can also be obtained in terms of the statistical moments defined by

$$\mu_l(p)\equiv\sum_n{}'(E_{Tn}-E_{T0})^p|(\psi_{T0},J_l\psi_{Tn})|^2.$$

[17] R. Sugar and R. Blankenbecler, Phys. Rev. **136**, B472 (1964).
[18] L. Spruch and Y. Hahn, Bull. Am. Phys. Soc. **12**, 560 (1967); also (to be published).

Many of these moments can be related to physical quantities and can therefore be extracted from experiment and some have rather simple mathematical properties. Thus, we have

$$\mu_1(-1)=(2e^2)^{-1}\alpha_1,\ \mu_2(-1)=(2e^2)^{-1}\alpha_2,\ \mu_1(-2)=\beta_1/e^4,$$

while $\mu_1(0)$ is related at least in the Hartree-Fock approximation to the matrix element that determines the ground-state diamagnetic susceptibility and $\mu_1(2)$ can be related to the mean-square momentum of the electrons in the ground state. The value of $\mu_1(1)$ can be obtained from the standard sum rule.

As in Subsec. C, we can obtain bounds on β_1 by obtaining mathematical inequalities involving β_1 and experimentally determinable quantities. Thus, using the Schwarz inequality and the relations $E_{Tn}-E_{T0}\geq 0$, we find

$$\mu_1^2(-1)/\mu_1(0)\leq\mu_1(-2)\leq\mu_1(-1)/(E_{T1}-E_{T0}).$$

If $\mu_1(0)$ is not known experimentally, it can be eliminated by the use of the inequality

$$\mu_1^2(0)\leq\mu_1(1)\mu_1(-1).$$

Many other such inequalities can be obtained.

Note added in proof. Professor Dalgarno has called our attention to a tabulation of $S(-3)=\mu_1(-2)$ for the rare-gas atoms by Kingston. [See R. J. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 88, 901 (1966).] The values for all but Xe should be accurate to within 10%; that for He should be better. In units of a_0^4, Eq. (5.7) gives the estimates $\beta_1(\mathrm{He})\approx 0.706$, $\beta_1(\mathrm{Ne})\approx 1.3$, $\beta_1(\mathrm{Ar})\approx 8.3$, $\beta_1(\mathrm{Kr})\approx 14$, and $\beta_1(\mathrm{Xe})\approx 29$.

ACKNOWLEDGMENT

One of us (C. J. K.) would like to thank Long Island University for making time available for this research.

APPENDIX A: FORMULATION IN TERMS OF UNPERTURBED STATES

The equivalent one-body problem defined by (2.9) is valid for any projection operator which has the same asymptotic form as P_a. In particular, it is valid for P_a replaced by P, the projection operator on to the unperturbed target ground state, $\psi_{T0}(\mathbf{r})$. We then have

$$P[H+HG^QH-E]P\Psi=0, \tag{A1}$$

where $G^Q=QG^QQ$ is defined by

$$G^Q\equiv[Q(E-H)Q]^{-1} \tag{A2}$$

and by the boundary conditions that it be regular at the origin and vanish asymptotically. Since

$$PHQ=PV_{\mathrm{sh}}Q,\quad QHP=QV_{\mathrm{sh}}P,\quad \text{and}\quad PH_T=E_{T0}P,$$

(A1) reduces, on dropping a factor $\psi_{T0}\rangle$ on the left, to

$$[T(\mathbf{q})+\mathcal{U}-E']u_0(\mathbf{q})=0, \tag{A3}$$

where

$$u_0(\mathbf{q})\equiv\int\psi_{T0}(\mathbf{r})\Psi(\mathbf{r},\mathbf{q})d\mathbf{r} \tag{A4}$$

and

$$\mathcal{U}u_0(\mathbf{q})=\int\psi_{T0}(\mathbf{r})[V_{\mathrm{unsh}}(q)+V_{\mathrm{sh}}(\mathbf{r},\mathbf{q})]\psi_{T0}(\mathbf{r})d\mathbf{r}\times u_0(\mathbf{q})$$
$$+\int\psi_{T0}(\mathbf{r})V_{\mathrm{sh}}(\mathbf{r},\mathbf{q})G^Q(\mathbf{r},\mathbf{q};\mathbf{r}',\mathbf{q}')V_{\mathrm{sh}}(\mathbf{r}',\mathbf{q}')$$
$$\times\psi_{T0}(\mathbf{r}')u_0(\mathbf{q}')d\mathbf{r}d\mathbf{r}'d\mathbf{q}'. \tag{A5}$$

The integral in the first term in (A5) reduces to $V_{\mathrm{unsh}}(q)$ plus a term, that due to $V_{\mathrm{sh}}(\mathbf{r},\mathbf{q})$, which vanishes asymptotically with q because of the assumed spherical symmetry of $\psi_{T0}(\mathbf{r})$. To evaluate the second term in (A5), we write

$$G^Q=G_0^Q+G_0^QUG^Q,$$

where

$$U\equiv Q(T+V_{\mathrm{sh}}+V_{\mathrm{unsh}}-E')Q,$$

and where $G_0^Q(\mathbf{r},\mathbf{r}')$ is defined as that solution of

$$Q(H_T-E_{T0})QG_0^Q=-Q\delta(\mathbf{r}-\mathbf{r}') \tag{A6}$$

which is regular at the origin, vanishes as $r\to\infty$, and is symmetric in $\mathbf{r}$ and $\mathbf{r}'$. Since $g_0(\mathbf{r},\mathbf{r}')$ was taken to be orthogonal to $\psi_{T0}(\mathbf{r})$ [and to $\psi_{T0}(\mathbf{r}')$], so that $g_0=Qg_0=g_0Q=Qg_0Q$, it follows from Eqs. (3.2) and (A6) that G_0^Q is nothing but g_0. Choosing q to be sufficiently large, the expansion

$$G^Q=g_0+g_0Ug_0+g_0Ug_0Ug_0+\cdots$$

will converge and we have, neglecting short-range components,

$$\mathcal{U}u_0(\mathbf{q})=V_{\mathrm{unsh}}(q)u_0(\mathbf{q})+V_{\mathrm{ad}}(q)u_0(\mathbf{q})$$
$$+\mathcal{U}_2u_0(\mathbf{q})+\cdots, \tag{A7}$$

where, using (2.3) and (3.16),

$$V_{\mathrm{ad}}(q)=\int\psi_{T0}(\mathbf{r})V_{\mathrm{sh}}(\mathbf{r},\mathbf{q})g_0(\mathbf{r},\mathbf{r}')V_{\mathrm{sh}}(\mathbf{r}',\mathbf{q})\psi_{T0}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$
$$\to(ee')^2\sum_l\frac{1}{q^{2l+2}}(\psi_{T0},J_lg_0J_l\psi_{T0})$$
$$=-\tfrac{1}{2}(e')^2\sum_l\frac{\alpha_l}{q^{2l+2}}. \tag{A8}$$

$V_{\mathrm{ad}}(q)$ is the adiabatic interaction to second order in the perturbation $V_{\mathrm{sh}}(\mathbf{r},\mathbf{q})$. The nonlocal interaction $\mathcal{U}_2$ is defined by

$$\mathcal{U}_2u_0(\mathbf{q})=\int\psi_{T0}V_{\mathrm{sh}}g_0Ug_0V_{\mathrm{sh}}\psi_{T0}d\mathbf{r}d\mathbf{r}'d\mathbf{r}''u_0(\mathbf{q})+\cdots.$$

Each of the V_{sh} terms explicitly exhibited contributes at most $1/q^2$ while the V_{sh} within U contributes at most a $1/q^3$ factor, since the relevant states in each of the g_0 factors are target states of angular momentum 1 or more. The V_{sh} term in U therefore contributes at most

a $1/q^7$ term to $\mathcal{U}_2$ and can be dropped. Replacing the other $V_{\rm sh}$ terms by J_1/q^2, we can write

$$\mathcal{U}_2 u_0(\mathbf{q}) = (ee')^2 q^{-2} \int \psi_{T0}(\mathbf{r}) J_1(\mathbf{r},\hat{q}) g_0(\mathbf{r},\mathbf{r}') \times g_0(\mathbf{r}',\mathbf{r}'') \psi_{T0}(\mathbf{r}'') A(\mathbf{q},\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' + O(q^{-7}), \quad \text{(A9)}$$

where

$$A(\mathbf{q},\mathbf{r}'') = [T(\mathbf{q}) + V_{\rm unsh}(q) - E'] \times \{[J_1(\mathbf{r}'',\hat{q})/q^2] u_0(\mathbf{q})\}. \quad \text{(A10)}$$

Since the point $q=0$ is not under consideration, we can use Eq. (3.19),

$$T(\mathbf{q})[J_1(\mathbf{r}'',\hat{q})/q^2] = 0.$$

Since

$$[T(\mathbf{q}) + V_{\rm unsh}(q) - E'] u_0(\mathbf{q}) = O(q^{-4}) u_0(\mathbf{q}),$$

on setting $J_1(\mathbf{r}'',\hat{q}) = \mathbf{r}'' \cdot \hat{q}$, we arrive at

$$A(\mathbf{q},\mathbf{r}'') = -2\frac{\hbar^2}{2m} J_1(\mathbf{r}'',\hat{q}) \left[\frac{d}{dq}\frac{1}{q^2}\right]\left[\frac{\partial}{\partial q} u_0(\mathbf{q})\right] - 2\frac{\hbar^2}{2m}\frac{\mathbf{r}''}{q^4}(1-\mu^2)\left[\frac{\partial}{\partial \mu}(\hat{r}''\cdot\hat{q})\right] \times \left[\frac{\partial}{\partial \mu} u_0(\mathbf{q})\right] + O(q^{-6}), \quad \text{(A11)}$$

where $\mu = \hat{k}\cdot\hat{q}$, with $\hat{k}$ being a fixed unit vector. When (A11) is inserted into (A9), the second term on the right-hand side of (A11) does not contribute. This can be seen easily by expanding the factor $(\hat{r}\cdot\hat{q})$ in $J_1(\mathbf{r},\hat{q})$ as

$$(\hat{r}\cdot\hat{q}) = \tfrac{4}{3}\pi \sum_m Y_{1m}^*(\hat{k},\hat{r}) Y_{1m}(\mu),$$

expanding $(\hat{r}''\cdot\hat{q})$ in a similar fashion, and then noting that, after the $d\mathbf{r}d\mathbf{r}'d\mathbf{r}''$ integrations, the $Y_{1m}(\mu)$ factor from $J_1(\mathbf{r},\hat{q})$ and the $(\partial/\partial\mu)Y_{1m}^*(\mu)$ factor from $(\hat{r}''\cdot\hat{q})$ combine and sum over m to vanish. Using (3.8) and (3.12), we remain with

$$V_2 u_0(q) = \frac{2\hbar^2(e')^2\beta_1}{me^2 q^5}\frac{d}{dq} u_0(q) + O\left(\frac{1}{q^7}\right). \quad \text{(A12)}$$

To get $\mathcal{U}_2$ into Hermitian form, we recognize that $\mathcal{U}_2$ is sufficiently weak that it is legitimate, to the order in $1/q$ under consideration, to replace it by a local potential which gives the same result as $\mathcal{U}_2$ does in the Born approximation. Thus, integrating by parts and dropping the surface term at $q=R$ since any contribution from a finite distance represents the effect of a short-range interaction, we have, for all angular momenta and for scattering by a neutral atom or an ion,

$$\int_R^\infty \frac{u_0}{q^5}\left(\frac{d}{dq} u_0\right) q^2 dq = \frac{1}{2}\int_R^\infty \frac{1}{q^3}\frac{d}{dq} u_0^2 dq \simeq \frac{3}{2}\int_R^\infty \frac{u_0^2}{q^6} q^2 dq.$$

This justifies the replacement of

$$\frac{1}{q^5}\frac{d}{dq} u_0(q)$$

by

$$\frac{3}{2q^6} u_0(q)$$

in (A12), and leads to

$$\mathcal{U}_2 = \mathcal{U}_2(q) = \frac{3\hbar^2(e')\beta_1}{me^2 q^6} + O\left(\frac{1}{q^7}\right). \quad \text{(A13)}$$

The use of Eqs. (A5), (A12), and (A13) leads to the same expression for $\mathcal{U}(q)$ as that found previously for $\mathcal{U}_a(q)$ in (1.1).

APPENDIX B: ASYMPTOTIC CONTRIBUTIONS OF v_0''

The operator v_0'' is defined by Eq. (2.20). To study its asymptotic contribution, we begin by introducing an approximation $\tilde{G}^{Q_a}$ to G^{Q_a}, where $\tilde{G}^{Q_a}$ is defined by

$$\tilde{G}^{Q_a} = \{Q_a[E_{T0} - H_T(\mathbf{r}) - V_{\rm sh}(\mathbf{r},\mathbf{q})]Q_a\}^{-1}, \quad \text{(B1)}$$

or, equivalently,

$$\tilde{G}^{Q_a}(\mathbf{r},\mathbf{q};\mathbf{r}',\mathbf{q}') = \sum_n{}' \frac{\phi_n(\mathbf{r},\mathbf{q})\rangle\langle\phi_n(\mathbf{r}',\mathbf{q})}{E_{T0} - \mathcal{E}_n(q)}\delta(\mathbf{q}-\mathbf{q}'). \quad \text{(B2)}$$

Use of the standard identity

$$\frac{1}{A} = \frac{1}{B} + \frac{1}{B}(B-A)\frac{1}{A}$$

leads to

$$G^{Q_a} = \tilde{G}^{Q_a} - \tilde{G}^{Q_a} Q_a [T(\mathbf{q}) + V_{\rm unsh}(q) - E'] Q_a G^{Q_a}. \quad \text{(B3)}$$

We can approximate $\mathcal{E}_n(q)$ by E_{Tn}, since this introduces an error of order $1/q^4$, and the error term will be multiplied by terms which themselves go faster than $1/q^4$. Using Eq. (B1) in (2.20), we arrive at

$$v_0'' u_{0a}(q) = \sum_n{}' (E_{T0} - E_{Tn})^{-1} \int\int \phi_0(\mathbf{r},\mathbf{q}) \times T(\mathbf{q})\phi_n(\mathbf{r},\mathbf{q})\phi_n(\mathbf{r}',\mathbf{q}) T(\mathbf{q})\phi_0(\mathbf{r}',\mathbf{q}) u_{0a}(\mathbf{q}) d\mathbf{r} d\mathbf{r}'$$

plus higher-order terms. The results

$$[T\phi_0] = O(q^{-6}) \quad \text{and} \quad (\partial\phi_0/\partial q) = O(q^{-3})$$

follow from Eqs. (3.18) and (3.14), respectively. The asymptotic q dependence of ϕ_n is similar in form to that of ϕ_0, and similar results follow for $[T\phi_n]$ and for $(\partial\phi_n/\partial q)$. We further use the results that $(\partial u_{0a}/\partial q)$ and $(\partial^2 u_{0a}/\partial q^2)$ are, for present purposes, proportional to ku_{0a} and $k^2 u_{0a}$, respectively; the argument is the same as that used in Appendix A. Because of the orthogonality of ϕ_0 and ϕ_n, at most two of the four derivatives can operate on u_{0a}, and the leading term of v_0'' is therefore of order q^{-8}.