

Two-Coulomb-exchange potential in the presence of open channels

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We use the techniques of dispersion theory to study the long-range behavior of the two-Coulomb-exchange potential acting between two atoms, or between an atom and a charged system such as an ion or electron, in the presence of open channels. In contrast to earlier work, we avoid the use of a multipole expansion. We focus on the case of atoms in initial S states. When one of the systems is in an excited state or the relative kinetic energy is large enough to allow excitation, the potential has an imaginary part that falls off exponentially with distance in the absence of degeneracy and as an inverse power in the presence of degeneracy of the initial state. The asymptotic form of the real part is unchanged from that found in the closed-channel case.

I. INTRODUCTION

The simplest approximation to the effective potential describing the low-energy interaction of two neutral spinless atoms A and B , each in an S -wave ground state, is the London potential V_L . This potential, valid for separations R which are large compared to atomic sizes but small compared to distances at which retardation is important, has the form

$$V_L = -C_L/R^6, \quad (1)$$

where C_L is the London constant. The London potential arises from the use, in second-order perturbation theory, of the dipole approximation to the electrostatic potential U , defined as the sum of the Coulomb interactions between the constituents of the two atoms. In the language of (Coulomb-gauge) quantum electrodynamics V_L can be thought of as arising from the exchange of two "Coulomb photons"; the exchange of a single photon only gives rise to a short-range force. The derivation of V_L is discussed in many texts and the problem of the evaluation of C_L , as well as the study of corrections to V_L , are the subject of a large literature.^{1,2}

Now suppose that, say, atom A is in an excited state. Then, in the absence of accidental degeneracy, the familiar expression for C_L as a sum of squares of dipolelike matrix elements divided by an energy difference remains well defined. It is therefore reasonable to suppose that (1) still represents a good starting point for describing the low-energy scattering of this excited state of A and the ground state of B . However, now the effective potential must also have an imaginary part, to accommodate the open channel $A^* + B \rightarrow A + B$, where A^* denotes the atom A in an excited state. Similarly, if both atoms are in the ground state but the relative kinetic energy is

sufficient to allow excitation of one of the atoms, such an imaginary part must appear.

While there has been some discussion of the question of the modifications needed when there are open channels, at least for the case when one of the initial states has $L \neq 0$,³ a systematic study has not been carried out. Moreover, the existence and precise nature of the imaginary part do not seem to have been addressed. The aim of this paper is to treat some aspects of these topics within a framework based on the techniques of dispersion theory. Most of the basic mathematical results needed for this purpose have already been presented and used in closely related work.⁴⁻⁶ These studies included the case of atom-atom scattering with each of the atoms in an initial S state almost degenerate with a state of opposite parity⁴ and electron-atom scattering with an S -state target atom having a nearby P -state partner.⁵ In the absence of such degeneracy the effective potential for electron-atom scattering is of course the polarization potential

$$V_{\text{pol}} = -\alpha_E e^2 / 2R^4, \quad (2)$$

where α_E is the static polarizability of the atom. In both these studies use was made of the dipole approximation, which in the ordinary case (no open channels and no degeneracy) leads to (1) or (2). A generalization in which all multipoles are included has been described recently.⁶ In the present paper we avoid a multipole expansion altogether. Section II gives our analysis, Sec. III contains a discussion, and Sec. IV has concluding remarks. The connection with the multipole expansion is illustrated in the Appendix.

II. ANALYSIS

A. Preliminaries

Consider the elastic scattering of atoms A and B , with initial momenta \mathbf{p} and $-\mathbf{p}$ and final momenta \mathbf{p}' and

$-\mathbf{p}'$, respectively. Let U denote the total electrostatic interaction between the constituents of A and those of B . Then the part of the amplitude for the transition $|\mathbf{p}; a, b\rangle \rightarrow |\mathbf{p}'; a, b\rangle$ which arises from U in second-order perturbation theory is given by

$$T = \sum_{m,n} T_{mn}, \quad (3)$$

where

$$T_{mn} = (2\pi)^{-3} \int d\mathbf{k} \langle \mathbf{p}'; a, b | U | \mathbf{k}; m, n \rangle \times \langle \mathbf{k}; m, n | U | \mathbf{p}; a, b \rangle / (D_{mn} + i\epsilon). \quad (4)$$

Here $|a\rangle$ and $|b\rangle$ denote arbitrary bound states of the atoms and the sum is over both bound and continuum states $|m\rangle$ and $|n\rangle$, with energies W_m and W_n . The energy denominator D_{mn} is given by

$$D_{mn} = (W_a + W_b - W_m - W_n) + (\mathbf{p}^2 - \mathbf{k}^2) / 2m_{AB}, \quad (5)$$

where $m_{AB} = m_A m_B / (m_A + m_B)$ is the reduced mass of the atom-atom system; note that D_{mn} may be either positive or negative. As discussed in Ref. 4, for fixed p^2 the amplitude T will be an analytic function of $t = -\mathbf{Q}^2$, where $\mathbf{Q} = \mathbf{p}' - \mathbf{p}$ is the three-momentum transfer, with a nearest singularity at $t=0$. This singularity arises from the long-range character of the Coulomb potentials that enter the definition of U . Apart from an additive polynomial in t , the amplitude T can therefore be written in the form

$$T = T(p^2, t) = (1/\pi) \int_0^\infty dt' \sigma(p^2, t') / (t' - t), \quad (6a)$$

where the spectral function σ is defined by

$$\sigma(p^2, t) = (1/2i) [T(p^2, t + i\epsilon) - T(p^2, t - i\epsilon)], \quad (6b)$$

with the limit $\epsilon \rightarrow 0$ understood. The long-range part of the corresponding effective potential, defined as the Fourier transform of T with respect to \mathbf{Q} , is then given by

$$V(R; p^2) = (1/4\pi^2 R) \int_0^\infty dt \sigma(p^2, t) \exp(-t^{1/2} R). \quad (7)$$

The behavior of V at large distances is determined by that of the spectral function in the neighborhood of $t=0$. We now show how this can be studied without use of a multipole expansion of the matrix elements of U or commitment to a particular atomic model.

B. Reorganization of terms

Our approach is based on a simple generalization of that used in Ref. 4. The factors in the numerator of the integrand of (4) may be written in the form

$$\langle \mathbf{k}; m, n | U | \mathbf{p}; a, b \rangle = (4\pi e^2 / q^2) F_{mn; ab}(\mathbf{q}), \quad (8a)$$

$$\langle \mathbf{p}'; a, b | U | \mathbf{k}; m, n \rangle = (4\pi e^2 / q'^2) F_{ab; mn}(\mathbf{q}'), \quad (8b)$$

where $\mathbf{q} = \mathbf{k} - \mathbf{p}$, $\mathbf{q}' = \mathbf{p}' - \mathbf{k}$. The F 's in (8a) and (8b) are transition form factors, sums of products of terms of the form

$$\langle m | \exp(i\mathbf{q} \cdot \mathbf{r}) | a \rangle \times \langle n | \exp(-i\mathbf{q}' \cdot \mathbf{r}) | b \rangle,$$

with c and d ratios of the masses of the constituents to the total mass of each atom.^{4,6} The precise form of the F 's does not matter for the purpose at hand. What is important is that they are manifestly analytic functions of the components of \mathbf{q} and \mathbf{q}' in the neighborhood of zero values for these components.

We shall restrict our attention to the case where both $|a\rangle$ and $|b\rangle$ are S states. We then collect together all contributions from states of total energy $E_m + E_n$, i.e., degenerate in total energy with a given intermediate state $|m, n\rangle$, by defining

$$N_{mn}(\mathbf{q}', \mathbf{q}) = \sum_{\text{deg.}} F_{ab; mn}(\mathbf{q}') F_{mn; ab}(\mathbf{q}). \quad (9a)$$

Then by rotational invariance N_{mn} is a function only of q^2 , q'^2 , and $\mathbf{q} \cdot \mathbf{q}'$. It follows that N_{mn} is an analytic function of these variables or, equivalently, of the variables q^2 , q'^2 , and $t = -(q^2 + q'^2 - 2\mathbf{q} \cdot \mathbf{q}')$ in the neighborhood of zero:

$$N_{mn}(\mathbf{q}', \mathbf{q}) = N_{mn}(t; q^2, q'^2). \quad (9b)$$

The corresponding contribution to T from such states, denoted by S_{mn} , is then seen to be given, on use of (4), (8), and (9), by

$$S_{mn} = \sum_{\text{deg.}} T_{mn} = (4\pi e^2)^2 (2\pi)^{-3} \int d\mathbf{k} N_{mn}(t; q^2, q'^2) / D_{mn} q^2 q'^2. \quad (10)$$

Analysis shows that the singularity of S_{mn} at $t=0$ arises from the region of the integrand where both q^2 and q'^2 are near zero. We therefore write, in (10),

$$N_{mn}(t; q^2, q'^2) = N_{mn}(t) + [N_{mn}(t; q^2, q'^2) - N_{mn}(t)], \quad (11a)$$

where $N_{mn}(t)$ is defined by

$$N_{mn}(t) \equiv N_{mn}(t; 0, 0). \quad (11b)$$

Then S_{mn} assumes the form

$$S_{mn} = S'_{mn} + S''_{mn}, \quad (12)$$

where S'_{mn} represents the contribution of the first term in (11a) and S''_{mn} that of the second term (in square brackets) in (11a). Note that in the dipole approximation N_{mn} is simply proportional to $\mathbf{q} \cdot \mathbf{q}'$, so that the second term in (11a) becomes proportional to $q^2 + q'^2$. This leads to a divergence in the integral defining S''_{mn} and thus to the introduction of a high-energy cutoff. In the present approach no such artifice is needed: the separation introduced by (11a) isolates the part S'_{mn} of S_{mn} that contributes to the long-range part of the potential without introducing a spurious divergence in the part S''_{mn} , which contributes only to the short-range part. On defining a quantity Δ_{mn} by

$$\Delta_{mn} = 2m_{AB}(W_m + W_n - W_a - W_b), \quad (13)$$

we may write S'_{mn} in the form

$$S'_{mn} = (4e^4 m_{AB} / \pi) N_{mn}(t) K(p^2, \Delta_{mn}; t), \quad (14)$$

with

$$K(p^2, \Delta; t) = \int dk (p^2 - \Delta - k^2 + i\epsilon)^{-1} (q^2 q'^2)^{-1}. \quad (15)$$

C. Spectral function near $t = 0$

Since S'_{mn} is analytic near $t = 0$, we may focus on S'_{mn} and because $N_{mn}(t)$ is also analytic at $t = 0$, the discontinuity $[S'_{mn}]_t$ of S'_{mn} across the branch cut starting at $t = 0$ is determined by that of the function K . Let σ'_{mn} denote the contribution to the spectral function arising from S'_{mn} . Then

$$\sigma'_{mn} = [S'_{mn}]_t / 2i \quad (16a)$$

and from (14) we have

$$[S'_{mn}]_t = (4e^4 m_{AB} / \pi) N_{mn}(t) [K(p^2, \Delta_{mn}; t)]_t. \quad (16b)$$

On combining the factors $1/q^2$ and $1/q'^2$ in (15) with a Feynman parameter and carrying out the angular integration one obtains^{4,7}

$$K(p^2, \Delta; t) = 4\pi \int_0^\infty dk (p^2 - \Delta - k^2 + i\epsilon)^{-1} \int_0^1 du F^{-1}, \quad (17a)$$

with

$$F = t_1 - (1 - u^2)t, \quad t_1 = (p^2 - k^2)^2 / k^2. \quad (17b)$$

The function defined by (17) has been studied and evaluated previously.^{4,7} One first separates K into an absorptive and a dispersive part, K_{abs} and K_{disp} , corresponding to the contribution of the δ function and principal value parts of the integral over k , respectively:

$$K = K_{\text{disp}} + iK_{\text{abs}}, \quad (18a)$$

where

$$K_{\text{abs}} = -4\pi^2 \int_0^\infty dk \delta(k_0^2 - k^2) \int_0^1 du F^{-1}, \quad (18b)$$

$$K_{\text{disp}} = 4\pi P \int_0^\infty dk (k_0^2 - k^2)^{-1} \int_0^1 du F^{-1}, \quad (18c)$$

with

$$k_0^2 = p^2 - \Delta. \quad (18d)$$

From (18b) one sees that for $k_0^2 > 0$, K_{abs} is nonvanishing and one finds that K_{abs} is itself an analytic function of t with a branch point at $t = t_0$, where t_0 is the value of t_1 at $k = |k_0|$,

$$t_0 = \Delta^2 / |p^2 - \Delta|. \quad (19)$$

The discontinuity of K_{abs} across the cut extending from t_0 to infinity is given by

$$[K_{\text{abs}}]_t = -2i(\pi^3 / |k_0|) [t(t - t_0)]^{-1/2} \quad (k_0^2 > 0), \quad (20a)$$

and of course

$$[K_{\text{abs}}]_t = 0 \quad (k_0^2 < 0). \quad (20b)$$

These equations hold for either sign of Δ . For the

function K_{disp} a more elaborate analysis is needed.⁸ For $\Delta > 0$ and $k_0^2 > 0$, K_{disp} is analytic in the t plane cut from $t = 0$ to $t = t_0$, with a discontinuity across that cut given by

$$[K_{\text{disp}}]_t = -2i(\pi^3 / |k_0|) [t(t_0 - t)]^{-1/2} \quad (\Delta > 0, k_0^2 > 0), \quad (21a)$$

whereas if $\Delta > 0$ and $k_0^2 < 0$ one finds that K_{disp} is analytic in the t plane cut from $t = 0$ to $t = +\infty$, with discontinuity

$$[K_{\text{disp}}]_t = -2i(\pi^3 / |k_0|) [t(t_0 + t)]^{-1/2} \quad (\Delta > 0, k_0^2 < 0). \quad (21b)$$

If $\Delta < 0$, then necessarily $k_0^2 > 0$ and K_{disp} is analytic in the t plane cut from $t = 0$ to $t = t_0$ with discontinuity

$$[K_{\text{disp}}]_t = 2i(\pi^3 / |k_0|) [t(t_0 - t)]^{-1/2} \quad (\Delta < 0, k_0^2 > 0). \quad (21c)$$

In summary, if Δ is negative, as is the case when $|a, b\rangle$ is an excited state and the intermediate states $|m, n\rangle$ lie below $|a, b\rangle$ in energy, then (20a) and (21c) apply. If Δ is positive, as is the case when $|a, b\rangle$ is the ground state, and also $p^2 < \Delta$, then (20b) and (21b) apply, whereas if $p^2 > \Delta$ then (20a) and (21a) apply.

The spectral function $\sigma'_{mn}(p^2, t)$ is thus determined by (16), (18), (20), and (21) to have the form

$$\begin{aligned} \sigma'_{mn}(p^2, t) = & -(4\pi^2 e^4 m_{AB}) [N_{mn}(t) / |k_0| t^{1/2}] \\ & \times \{ \theta(k_0^2) [\theta(t_0 - t)(t_0 - t)^{-1/2} \epsilon(\Delta_{mn}) \\ & + i\theta(t - t_0)(t - t_0)^{-1/2}] \\ & + \theta(-k_0^2)(t_0 + t)^{-1/2} \}, \quad (22) \end{aligned}$$

where now $k_0^2 = p^2 - \Delta_{mn}$ and $t_0 = (\Delta_{mn})^2 / |p^2 - \Delta_{mn}|$. The corresponding contribution V'_{mn} to the long-range part of the potential is, according to (7), given by

$$V'_{mn}(R; p^2) = (1/4\pi^2 R) \int_0^\infty dt \sigma'(p^2, t) \exp(-t^{1/2} R). \quad (23)$$

III. DISCUSSION

A. Behavior of V'_{mn} for large R

It is convenient to consider separately the case where Δ_{mn} is nonvanishing and the case where it is zero or close to zero.

I. $\Delta_{mn} \neq 0$

We see from Eq. (22) that whatever the sign of Δ_{mn} and k_0^2 , the real part of the spectral function $\sigma'_{mn}(p^2, t)$ behaves as the product $N_{mn}(t)t^{-1/2}$ near $t = 0$. Now, as shown in Ref. 4, in the dipole approximation $N_{mn}(t)$ varies as t^2 near $t = 0$ and it is easy to see that this is true more generally: in an expansion in powers of t , for two neutral atoms in S states, we have

$$N_{mn}(t) = a_{mn}t^2 + b_{mn}t^3 + \dots, \quad (24)$$

with a_{mn} not equal to zero for states $|m\rangle$ and $|n\rangle$ which are dipole-connected to $|a\rangle$ and $|b\rangle$, respectively. It follows that the real part of the spectral function behaves as $t^{3/2}$ for t near 0 and this implies, via Eq. (23), that the large- R behavior of the real part of the corresponding effective potential will in all cases have the Wang-London R^{-6} form. To be precise, since $\Delta_{mn} \neq 0$ implies $t_0 \neq 0$, we can expand the right-hand side of (22) in powers of t for $t \ll t_0$. From the expansion (24) we obtain

$$\text{Re}\sigma'_{mn}(p^2, t) = -(4\pi^2 e^4 m_{AB})(a_{mn}/\Delta_{mn})t^{3/2} + \dots \quad (25)$$

Note that for the leading term, exhibited in (25), the various θ and ϵ functions have disappeared, along with the absolute value sign on Δ_{mn} . Substitution of (25) into (23) yields, on neglect of terms that fall off exponentially and use of the relation

$$\int_0^\infty dt t^{3/2} \exp(-t^{1/2}R) = (2)4!R^{-5},$$

the result

$$\text{Re}V'_{mn}(R; p^2) = -C'_{mn}/R^6 + \dots, \quad (26a)$$

where

$$C'_{mn} = 4!(e^4 m_{AB})(2a_{mn}/\Delta_{mn}). \quad (26b)$$

Each extra power of t in (24) will produce two more inverse powers of R in the corresponding contribution to the potential, so that (24) effectively generates a multipole expansion for the real part of the potential. An explicit illustration of this expansion is given in the Appendix, for the case of the scattering of two two-body composites.

In contrast, the imaginary part of $\sigma'_{mn}(p^2, t)$, associated with the $i(t-t_0)^{-1/2}$ term in (22), contributes only for $t > t_0$. The corresponding potential $\text{Im}V'_{mn}$ then falls off exponentially with R , with a (p -dependent) range equal to $t_0^{-1/2}$. To be specific, from (22) and (23) we obtain

$$\text{Im}V'_{mn}(R; p^2) = -(e^4 m_{AB}/|k_0|)R^{-1}I_{mn}(R; p^2), \quad (27a)$$

where

$$I_{mn}(R; p^2) = \int_{t_0}^\infty dt [t(t-t_0)]^{-1/2} \times N_{mn}(t) \exp(-t^{1/2}R). \quad (27b)$$

For large R we have

$$I_{mn} \sim [N_{mn}(t_0)/t_0^{1/2}] \int_{t_0}^\infty dt (t-t_0)^{-1/2} \times \exp(-t^{1/2}R) \quad (27c)$$

and the asymptotic form of the integral is given by

$$(2\pi)^{1/2} t_0^{1/4} \exp(-t_0^{1/2}R)/R^{1/2}. \quad (27d)$$

It follows that

$$\begin{aligned} \text{Im}V'_{mn}(R; p^2) &= -(2\pi)^{1/2} (e^4 m_{AB}/|k_0|) \\ &\times [N_{mn}(t_0)/t_0^{1/4}] \\ &\times \exp(-t_0^{1/2}R) R^{-3/2}. \end{aligned} \quad (28)$$

Of course, the discontinuity of the function S''_{mn} , which contributes only short-range terms to the real part of the potential, will also contribute such terms to the imaginary part of the potential.

2. $\Delta_{mn} \approx 0$

The situation is different if Δ_{mn} can be very small. This is obviously possible if either (i) both the initial states $|a\rangle$ and $|b\rangle$ are almost degenerate, so that there exist states $|m\rangle$ and $|n\rangle$ for which both $W_m - W_a$ and $W_n - W_b$ are nearly zero, or (ii) there exist states $|m\rangle$ and $|n\rangle$ such that $W_n - W_b \approx -(W_m - W_a)$. An example of the first type is provided by the scattering of positronium and a hydrogen atom, both in $2s$ states. An example of the second type is provided by the scattering of two atoms that happen to have two spectral lines that almost coincide in wavelength and are in appropriate initial states. Whatever the reason, from (22) we see that, on the one hand, there is in this case no contribution to the real part of V' (in the limit of vanishing Δ_{mn}) because $t_0 = 0$ and the domain over which the relevant step functions in (22) do not vanish shrinks to zero. Thus the leading term in $\text{Re}V'$ always behaves as R^{-6} for large R , with a coefficient determined by the transitions for which $\Delta \neq 0$. On the other hand, there still is a contribution $\text{Im}V'_{mn}$ to the imaginary part of V ; however, in the limit $\Delta_{mn} \rightarrow 0$ it now falls off only as an inverse power, rather than exponentially. To be more explicit, for states $|m\rangle$ and $|n\rangle$ that are dipole-connected to $|a\rangle$ and $|b\rangle$ we now have $\text{Im}\sigma'_{mn} \sim t$ for $t > 0$ and, correspondingly,

$$\text{Im}V_{mn} \sim m_{AB} e^4 a^4 / pR^5, \quad (29)$$

where a is a length of the order of atomic dimensions; if the states $|m, n\rangle$ are only connected to $|a, b\rangle$ by a higher-order multipole transition, the power of R in (29) will of course increase. In this context one should however note the caveat raised in Ref. 4 concerning the use of potentials in situations in which the scattering amplitude is strongly momentum dependent.

The result (29) is essentially the same as that obtained in Ref. 7 for the scattering of doubly degenerate S -state systems, i.e., each of which has a nearby P -state partner; the consequences for the phase shifts were explored there. However, it is perhaps easier to carry out an experiment in which one scatters an excited atom from a ground-state atom of the same type than one which requires two ground-state atoms with the necessary degeneracy.

B. Ion-atom scattering

Our general analysis is basically unchanged if one of the systems, say B , is charged, e.g., an ion or an electron. For B an ion, the function $N_{mn}(t)$ will vary as t rather than t^2 near $t=0$, for dipole-connected states, so that the real part of the effective potential will vary as R^{-4} for

large R and the imaginary part will again be short range, unless the exceptional circumstances described above obtain. For B a "point" particle, such as an electron, the double sum (3) is replaced by a single sum, $\sum T_m$, where T_m is obtained by deleting the symbols b and n in (4) and the symbols E_b and E_n in (5). The corresponding numerator function $N_m(t)$ then has properties similar to the atom-ion case and therefore so do the associated effective potentials. If both systems are charged, as in the case of ion-ion or electron-ion scattering, the numerator function has a nonzero limit as $t \rightarrow 0$, but the spectral function, although still well defined, now has a part that behaves as t^{-1} near $t = 0$; the logarithmic divergence that then arises in (7) is canceled when the iteration of the lowest-order effective potential is subtracted, as discussed in Ref. 7 in the context of field theory.

IV. CONCLUDING REMARKS

We have seen in the study of the elastic scattering problem for S states, on which we have focused here, that on the one hand the real part of the long-range effective potential arising from two-Coulomb exchange is found not to undergo any change from the London form, whether or not there is near degeneracy, as already found in Ref. 4 in the context of the dipole approximation, and whether or not there are open channels. On the other hand, in the presence of near degeneracy there is an imaginary part that can be substantial; under such circumstances it is not permissible to neglect the relative kinetic energy of the two atoms.

However, one may raise a question about the first-order effect of U , in the presence of degeneracy, often considered in the context of molecule formation. Suppose we consider the interaction of a H atom and deuterium, both in the $2s$ state. (We take the nuclei to be different to avoid complications from exchange effects.) In the limit of exact $2s$ - $2p$ degeneracy, application of the Born-Oppenheimer approximation to the computation of the second-order level shift arising from the electrostatic potential U , with the nuclei a fixed distance R apart, requires that one first diagonalize the matrix of U taken between the complex of product $|2s\rangle$ and $|2p\rangle$ states. Diagonalization of this matrix will yield a first-order shift for the $|2s, 2s\rangle$ state (now modified by mixing with $|2p, 2s\rangle$ states) that has a term decreasing as R^{-3} . There is no counterpart of this in the potential we have calculated, which is relevant for the purely elastic scattering of two atoms, because we are doing perturbation theory in the continuum. Diagonalization is both unnecessary and inappropriate: the boundary condition at large separations between the atoms is that each of them be in an S state, not in a linear combination of an S state and a P state; such a linear combination does not have a definite energy as long as the degeneracy is not exact.

Even for the calculation of energy shifts in the context of the adiabatic approximation, an energy shift of first order in U only occurs when the matrix elements of U , symbolized by $\langle U \rangle$, are much larger than the energy differences between the complex of states linked by U , symbolized by δ . Formally this occurs because the level

shifts have the form, in obvious symbolic notation,

$$\langle U \rangle^2 / (\delta^2 + \langle U \rangle^2)^{1/2}.$$

Since $\langle U \rangle$ decreases with R (as R^{-3} for the case considered above), for sufficiently large R and $\delta \neq 0$ the criterion for a first-order level shift is never satisfied.

In further study, it would be interesting to extend the approach used here to the scattering of systems with nonzero angular momentum.

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APPENDIX: TWO-COULOMB-EXCHANGE POTENTIAL FOR TWO-BODY COMPOSITES

1. Preliminaries

In this appendix we make the results of Sec. II more explicit, by considering the simple case where A is a two-body composite, with constituents 1 and 2, and B is a similar system with constituents 3 and 4. Let m_i and Q_i denote the masses and charge numbers of these constituents ($i = 1, 2, 3, 4$). The functions defined by Eqs. (8a) and (8b) of the text then have the form

$$F_{mn;ab}(\mathbf{q}) = G_{ma}(\mathbf{q})G_{nb}(\mathbf{q}), \quad (\text{A1a})$$

$$F_{ab;mn}(\mathbf{q}') = G_{am}(\mathbf{q}')G_{bn}(\mathbf{q}'), \quad (\text{A1b})$$

where the G 's are transition form factors defined by

$$G_{ma}(\mathbf{q}) = \langle m | Z_A(\mathbf{q} \cdot \mathbf{r}) | a \rangle, \quad (\text{A2a})$$

$$G_{nb}(\mathbf{q}) = \langle n | Z_B(-\mathbf{q} \cdot \mathbf{r}') | b \rangle, \quad (\text{A2b})$$

with

$$Z_A(\mathbf{q} \cdot \mathbf{r}) = Q_1 \exp(ic_2 \mathbf{q} \cdot \mathbf{r}) + Q_2 \exp(-ic_1 \mathbf{q} \cdot \mathbf{r}), \quad (\text{A2c})$$

$$Z_B(-\mathbf{q} \cdot \mathbf{r}') = Q_3 \exp(-ic_4 \mathbf{q} \cdot \mathbf{r}') + Q_4 \exp(ic_3 \mathbf{q} \cdot \mathbf{r}'). \quad (\text{A2d})$$

Here \mathbf{r} and \mathbf{r}' are the relative coordinates of the constituents of A and B, respectively, and the c 's are mass ratios defined by

$$c_1 = m_1/m_A, \quad c_2 = m_2/m_A,$$

$$c_3 = m_3/m_B, \quad c_4 = m_4/m_B.$$

It follows that the function N_{mn} defined by Eq. (9a) has the form

$$N_{mn}(\mathbf{q}, \mathbf{q}') = \sum_{\text{deg.}} [G_{am}(\mathbf{q}')G_{ma}(\mathbf{q})][G_{bn}(\mathbf{q}')G_{nb}(\mathbf{q})]. \quad (\text{A3})$$

where the sum is over all states degenerate with a given product state $|m, n\rangle$.

We restrict our attention to systems A and B bound by spherically symmetric interactions with initial states $|a\rangle$ and $|b\rangle$ of zero angular momentum and write the intermediate states $|m\rangle$ and $|n\rangle$ more explicitly in the form

$$|m\rangle = |\tilde{m}; L, m_L\rangle, \quad |n\rangle = |\tilde{n}; L', m_{L'}\rangle, \quad (\text{A4a})$$

with \tilde{m} a radial quantum number, L and m_L internal angular momentum quantum numbers, etc. In this notation the initial states have the form

$$|a\rangle = |\tilde{a}; 0, 0\rangle, \quad |b\rangle = |\tilde{b}; 0, 0\rangle. \quad (\text{A4b})$$

We now focus on the contribution to the right-hand side of (A3) which arises from the summation over the azimuthal quantum numbers m_L and $m_{L'}$, for fixed values of \tilde{m} , n , L , and L' ; we denote this quantity by $N_{mn}(\mathbf{q}, \mathbf{q}'; L, L')$. Then from (A3) we obtain

$$N_{mn}(\mathbf{q}, \mathbf{q}'; L, L') = N_m(\mathbf{q}, \mathbf{q}'; L) N_n(-\mathbf{q}, -\mathbf{q}'; L), \quad (\text{A5})$$

where

$$N_m(\mathbf{q}, \mathbf{q}'; L) = \sum_{m_L} \langle a | Z_A(\mathbf{q} \cdot \mathbf{r}) | \tilde{m}; L, m_L \rangle \times \langle \tilde{m}; L, m_L | Z_A(\mathbf{q}' \cdot \mathbf{r}) | a \rangle, \quad (\text{A6})$$

and $N_n(\mathbf{q}, \mathbf{q}'; L')$ is similarly defined. Because of the summation over m_L , N_m is a function only of the rotational invariants q^2 , q'^2 , and t :

$$N_m = N_m(t, q^2, q'^2; L). \quad (\text{A7})$$

2. Study of N_m

We only need the value of N_m at $q^2 = q'^2 = 0$ and therefore define

$$N_m(t; L) = N_m(t, 0, 0; L). \quad (\text{A8})$$

One way to get a fairly explicit expression for $N_m(t; L)$ is to follow a procedure used previously in a closely related context.⁶ On expanding the exponentials in (A6) in power series one obtains

$$N_m = \sum_k \sum_l (C_{A;k} C_{A;l} / k! l!) (i)^{k+l} I_{m;kl}(\mathbf{q}, \mathbf{q}'; L), \quad (\text{A9a})$$

where

$$C_{A;k} = Q_1(c_2)^k + Q_2(-c_1)^k \quad (\text{A9b})$$

and

$$I_{m;kl} = \sum_{m_L} \langle a | (\mathbf{q}' \cdot \mathbf{r})^k | \tilde{m}; L, m_L \rangle \langle \tilde{m}; L, m_L | (\mathbf{q} \cdot \mathbf{r})^l | a \rangle. \quad (\text{A9c})$$

On defining a tensor T by

$$T_{i_1 \dots i_k; j_1 \dots j_l} = \sum_{m_L} \langle a | x_{i_1} \dots x_{i_k} | \tilde{m}; L, m_L \rangle \times \langle \tilde{m}; L, m_L | x_{j_1} \dots x_{j_l} | a \rangle, \quad (\text{A9d})$$

where the x 's denote the Cartesian components of \mathbf{r} , we may write (A9c) in the form

$$I_{m;kl} = \sum_{i,j} (q'_{i_1} \dots q'_{i_k})(q_{j_1} \dots q_{j_l}) \times T_{i_1 \dots i_k; j_1 \dots j_l}, \quad (\text{A10})$$

where the summation is over repeated indices. It can be shown that the right-hand side of (A10) vanishes for $q^2 = q'^2 = 0$, unless $k = l = L$. Thus

$$N_m = (C_{A;L} / L!)^2 (-1)^L I_{m;LL} + O(q^2) + O(q'^2). \quad (\text{A11})$$

Next, we use the symmetry of T under separate permutations of the i or j indices to write

$$T_{i_1 \dots i_k; j_1 \dots j_l} = G_L(m) \sum_{\pi} \delta_{i_1 j_{\pi(1)}} \dots \delta_{i_k j_{\pi(k)}} + \dots, \quad (\text{A12a})$$

where the sum is over permutations π of $1, 2, \dots, L$ and the dots denote terms involving at least one Kronecker δ with two i indices or two j indices. The factor $G_L(m)$ in (A12) has the form

$$G_L(m) = c_L |\langle \tilde{a} | r^L | \tilde{m} \rangle|^2, \quad (\text{A12b})$$

with $\langle \tilde{a} | r^L | \tilde{m} \rangle$ a reduced matrix element that depends only on radial wave functions and c_L defined by

$$c_L = 4\pi 2^L L! / (2L + 1)!. \quad (\text{A12c})$$

On substituting the form (A12) into (A10) with $k = l = L$ we obtain

$$I_{m;LL} = G_L(m) (\mathbf{q} \cdot \mathbf{q}')^L L! + O(q^2) + O(q'^2). \quad (\text{A13})$$

Substitution of (A13) into (A11) together with use of the fact that $\mathbf{q}' \cdot \mathbf{q} = t/2$ when $q^2 = q'^2 = 0$, we find that

$$N_m(t; L) = (C_{A;L} / L!)^2 (-1)^L G_L(m) L! (t/2)^L. \quad (\text{A14a})$$

Similarly we obtain

$$N_n(t; L') = (C_{B;L'} / L'!)^2 (-1)^{L'} G_{L'}(n) L'! (t/2)^{L'}. \quad (\text{A14b})$$

3. Form of the potential

From (A5), (A7), and (A8) we see that for $q^2 = q'^2 = 0$, the contribution to N_{mn} from intermediate states $|m\rangle$ of A and $|n\rangle$ of B, with angular momentum L and L' , respectively, is given by

$$N_{mn}(t; L, L') = N_m(t; L) N_n(t; L'). \quad (\text{A15})$$

On use of (A14), this takes the form

$$N_{mn}(t; L, L') = a_{mn}(L, L') t^{L+L'}, \quad (\text{A16a})$$

where

$$a_{mn}(L, L') = (C_{A;L})^2 (C_{B;L'})^2 (-\frac{1}{2})^{L+L'} \times G_L(m) G_{L'}(n) / L! L'!. \quad (\text{A16b})$$

Note that if there is no accidental degeneracy, the values of L and L' are determined by the energies E_m and E_n .

On replacing N_{mn} in (22) by (A16a) and substituting

the result into Eq. (23), one obtains a potential $V'_{mn}(R;p^2;L,L')$ defined by

$$V'_{mn}(R;p^2;L,L') = -e^4 m_{AB} a_{mn}(L,L')/|k_0|R \\ \times [\theta(\Delta_{mn} - p^2)X_{L+L'} \\ + \theta(p^2 - \Delta_{mn})\epsilon(\Delta_{mn})Y_{L+L'} \\ + i\theta(p^2 - \Delta_{mn})Z_{L+L'}], \quad (\text{A17})$$

where

$$X_k = \int_0^\infty dt \exp(-t^{1/2}R)t^{k-1/2}(t_0+t)^{-1/2}, \quad (\text{A18a})$$

$$Y_k = \int_0^{t_0} dt \exp(-t^{1/2}R)t^{k-1/2}(t_0-t)^{-1/2}, \quad (\text{A18b})$$

$$Z_k = \int_{t_0}^\infty dt \exp(-t^{1/2}R)t^{k-1/2}(t-t_0)^{-1/2}. \quad (\text{A18c})$$

With $t = t_0 x^2$, Eqs. (A18b)–(A18d) take the form

$$X_k = 2 \left[\frac{-d}{dR} \right]^{2k-1} X(z), \quad (\text{A19a})$$

$$Y_k = 2 \left[\frac{-d}{dR} \right]^{2k-1} Y(z), \quad (\text{A19b})$$

$$Z_k = 2 \left[\frac{-d}{dR} \right]^{2k-1} Z(z), \quad (\text{A19c})$$

where

$$X(z) = \int_0^\infty dx \exp(-zx)x(1+x^2)^{-1/2}, \quad (\text{A20a})$$

$$Y(z) = \int_0^1 dx \exp(-zx)x(1-x^2)^{-1/2}, \quad (\text{A20b})$$

$$Z(z) = \int_1^\infty dx \exp(-zx)x(x^2-1)^{-1/2}, \quad (\text{A20c})$$

and

$$z = t_0^{1/2}R. \quad (\text{A21})$$

The integrals on the right-hand side of Eqs. (A20a)–(A20c) can be expressed as linear combinations of various cylinder functions, viz., the modified Bessel functions N_1 , I_1 , and K_1 , and the Struve functions H_1 and L_1 ,^{9,10}

$$X(z) = (\pi/2)[H_1(z) - N_1(z)] - 1, \quad (\text{A22a})$$

$$Y(z) = (\pi/2)[L_1(z) - I_1(z)] + 1, \quad (\text{A22b})$$

$$Z(z) = K_1(z). \quad (\text{A22c})$$

Equation (17), together with the definitions and relations (A18)–(A22), is the main result of this appendix. We now use it to obtain the behavior of V'_{mn} for large and small values of z .

For large values of z , one has the asymptotic expansions

$$X(z) \sim \frac{1}{2} \sum_{k=1}^{\infty} [\Gamma(k + \frac{1}{2})/\Gamma(-k + \frac{3}{2})](z/2)^{-2k} \quad (\text{A23a})$$

and

$$Y(z) \sim \frac{1}{2} \sum_{k=1}^{\infty} (-1)^{k+1} [\Gamma(k + \frac{1}{2})/\Gamma(-k + \frac{3}{2})](z/2)^{-2k}, \quad (\text{A23b})$$

so that, on carrying out the indicated differentiations in (A19), one obtains a multipole expansion for the real part of V'_{mn} :

$$\text{Re}V'_{mn}(R;L,L') = -e^4 m_{AB} a_{mn}(L,L') \sum_{k=1}^{\infty} \frac{\Gamma(k + \frac{1}{2})2^{2k}[2(k+L+L'-1)]!}{\Gamma(-k + \frac{3}{2})(2k-1)!(\Delta_{mn})^{2k-1}} (\Delta_{mn} - p^2)^{k-1} R^{-2(L+L'+k)}. \quad (\text{A24})$$

Note that the form of the right-hand side of (A24) is independent of the signs of Δ_{mn} and $p^2 - \Delta_{mn}$. For $L = L' = 1$, the $k = 1$ term yields the usual contribution to the London potential, associated with intermediate P states, while the terms with $k > 1$ give the nonadiabatic and energy-dependent corrections.

If the quantity z is not large compared to unity, (A24) is not valid and the form of the associated potential does depend on the sign of $p^2 - \Delta_{mn}$. This is relevant if one of the possible values of Δ_{mn} is very small. For small values of z , the functions $H_1(z)$, $I_1(z)$, and $L_1(z)$ all vary as non-negative integral powers of z , whereas $N_1(z)$ and $K_1(z)$ vary as z^{-1} . In this case the leading terms come from differentiation of these latter functions. For small z one has $-(\pi/2)N_1(z) \sim z^{-1}$ and $K_1(z) \sim z^{-1}$, so that one obtains

$$V'_{mn}(R;p^2,L,L') = -2e^4 m_{AB} a_{mn}(L,L')(2L+2L'-1)! R^{-2(L+L')-1} [\theta(\Delta_{mn} - p^2)(\Delta_{mn} - p^2)^{-1/2} \\ + i\theta(p^2 - \Delta_{mn})(p^2 - \Delta_{mn})^{-1/2}]. \quad (\text{A25})$$

If only dipole interactions are taken into account, the contribution to the atom-electron potential ($L = 1, L' = 0$) of the states for which Δ_{mn} is very small varies as R^{-3} and is real for $\Delta_{mn} > p^2$ whereas it is purely imaginary, with the same power behavior, for $p^2 > \Delta_{mn}$. For the atom-atom potential ($L = L' = 1$) the behavior is similar, but with R^{-3} replaced by R^{-5} . This is consistent with earlier findings.^{5,7} The present result, Eq. (A17), has the advantage of being in closed form, valid for all values of R .

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