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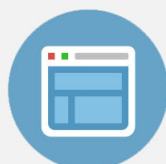
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# Angular momentum coupling schemes in the quantum mechanical treatment of $P$ -state atom collisions

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For the multichannel Schrödinger equations which arise in the quantum mechanical close coupling treatment of atomic collisions involving fine structure effects, alternative representations are developed by angular momentum algebra. The various representations are closely related to Hund's coupling schemes for rotating diatomic molecules. Matrix elements for the electrostatic interaction and for the orthogonal transformations which connect the various representations, are given explicitly for the case when only one atom has internal angular momenta and follows  $LS$  coupling. The limit of large angular momenta, of interest under semiclassical conditions, is also considered. Some examples of applications to  $P$  atom collisions are discussed.

## I. INTRODUCTION

The recent developments of molecular beam techniques are beginning to yield an increasing amount of information on collisions of atoms not in  $S$  states, in particular  $P$  atoms: Both elastic<sup>1</sup> and intramultiplet mixing cross sections<sup>2</sup> are now being measured, thereby stimulating the interest in a quantum mechanical approach where fine structure effects are explicitly taken into account.

In the past, bulk experiments on collisional quenching of resonance radiation, pressure shift and broadening of linewidths, depolarization, orientation, and so on, promoted the development of successful semiclassical treatments of  $P$  atom collisions<sup>3</sup>: These treatments are often useful for predicting collision cross sections, such as are now needed in disparate fields as astrophysics or laser technology.

However, the applications appear to demand a more rigorous approach to the dynamics, and the experiments are definitely showing that quantum mechanical effects contain detailed information on atomic interactions. On the other hand, quantum chemical calculations are reaching the stage that reliable characterization of the interatomic forces can be obtained, but at the expense of big computational efforts, and within error limits often difficult to assess. It is therefore hoped that the experiments on atomic collisions, which have been proven of great value for the measurements of weak interatomic forces between  $S$  atoms, will soon provide information of comparable quality about atoms carrying internal angular momentum.

The proper quantum mechanical treatment of these collisions requires the close coupling expansion over at least the atomic fine structure components, and therefore leads to sets of coupled differential equations. Even though the limits imposed on the expansion basis make these sets not unmanageable by present numerical techniques, the involved partial waves are typically so many that the computation of cross sections with assumed interactions is a very time consuming effort. In the analysis of the experimental data, the standard procedure consists of varying parts of the assumed interactions, until a satisfactory reproduction of measured quantities is achieved. The complexity of such a pro-

cedure has suggested that we look more carefully into the very structure of the close coupling equations, in order to exploit the connections between the nature of the interactions and their manifestation in the observables.

As a first step in this direction, we found it interesting to seek for alternative expansions for the total scattering wave function, which could have specific advantages, depending on the relative role played by the relevant interactions. Specifically, we were guided by the work of Nikitin and others,<sup>3</sup> who have shown that, within the semiclassical framework, the consideration of alternative angular momentum coupling schemes gave a physically sound view of the collision process, and could lead to the development of reasonable approximations to the dynamics. Their idea is that, by considering the relative role of relevant interactions at a given impact parameter and interatomic distance, the collision diatom can be best described by coupling schemes, similar to those introduced more than 50 years ago by Hund in the spectroscopy of the rotating diatomic molecules.<sup>4</sup>

The same idea is applied in this work to the quantum mechanical treatment: After an outlook in the next section of the close coupling formalism, we derive in Sec. III the angular momentum machinery for obtaining alternative representations for the coupled equations, and in Sec. IV the limiting forms which are obtained for large angular momenta. Then, in Sec. V, as typical examples of the working of this approach, we consider explicitly collisions of  $^1P$ ,  $^2P$ , and  $^3P$  atoms with  $^1S$  species, although the treatment is not restricted to these cases. Finally, in Sec. VI, a brief discussion will be given of possible extensions of these methods, and of their use for the development of accurate approximation schemes. Computational examples and an overall assessment of some of these approximations will be presented in the accompanying paper.<sup>5</sup>

## II. THE CLOSE COUPLING EQUATIONS

### A. The space-fixed representation

In the quantum mechanical calculation of atomic collision processes, one has to solve a multichannel Schrödinger equation, which can be obtained by expand-

ing the total scattering wave function in eigenfunctions of the total angular momentum  $J$ . In matrix form, this equation can be written, for each  $J$ ,

$$\left[ \left( \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E \right) \mathbf{1} - U(R) \right] \mathbf{u}(R) = 0, \quad (2.1)$$

where  $E$  is the collision energy and  $\mu$  is the reduced mass of the two atoms.

The matrix of radial functions  $\mathbf{u}(R)$ , which depend on the interatomic distance  $R$ , and must obey to proper boundary conditions as  $R$  is zero and as it goes to infinity, are to be found for each  $J$ : Their asymptotic large  $R$  behavior allows the construction of the  $S$  matrix, which in turn contains all of the information needed to compute all the observables. The  $u$  and  $S$  matrices, as well as the symmetric effective potential matrix  $U$ , all depend on the expansion basis chosen for the total scattering wave function. The choice of the basis will therefore also determine the boundary conditions for Eq. (2.1), and the connection between the scattering matrix and the cross sections.

For the treatment of collisions between atoms, which we assume in the following to be described by  $LS$  coupling, when only fine structure states are introduced in the close coupling expansion, the effective potential  $U$ , whose off-diagonal matrix elements provide the coupling for Eq. (2.1), will be considered as the sum of three terms:

$$U(R) = \mathcal{E} + \hbar^2 \mathbf{l}^2 / 2\mu R^2 + V(R), \quad (2.2)$$

representing spin-orbit, rotational, and electrostatic interactions, respectively.

The  $\mathcal{E}$  matrix, which contains the magnetic interactions, at sufficiently large distances has eigenvalues which are given by the energy levels of  $j_i$  states of each of the two atoms, where  $j_i = L_i + S_i$ ,  $L_i$  being the atomic orbital momentum quantum number of atom  $i$ , and  $S_i$  its spin. This asymptotic level splitting is a consequence of spin-orbit interaction within each atom, and the customary practice we shall follow is to consider it as constant even at finite interatomic distances. Accordingly, the matrix  $\mathcal{E}$  will be diagonal in any representation where the atomic  $j$ 's are defined and its elements will then be the threshold energies of the various channels.

The second term in Eq. (2.2) is the matrix representation of the centrifugal operator, and its eigenvalues  $l(l+1)/2\mu R^2$  are labeled by the orbital quantum number for the collision  $l$ . The values for the latter are bound by the triangular condition which results from  $l = J - j$ , where  $j$  is the vector sum of  $j_i$ 's. Because of these properties of the first two terms in Eq. (2.2), a natural choice for the expansion basis of the total wave function is in terms of eigenfunctions of  $\mathbf{j}^2$  and  $\mathbf{l}^2$ . This leads to the so-called space fixed representation for Eq. (2.1), which we denote by  $|jl\rangle$ , dropping from the notation any appearance of  $J, L$ , and  $S$ , which are assumed to be constant. Boundary conditions for this basis are well known, as are well known the connection between the asymptotic behavior of  $\mathbf{u}(R)$  and the scattering matrix, and that between the latter and cross sections.<sup>6,7</sup>

## B. The electrostatic interaction

In this  $|jl\rangle$  representation, the matrix of electrostatic interaction  $V$  is in general not diagonal, and its off-diagonal elements provide the coupling for Eq. (2.1). However, we know from the theory of diatomic molecules<sup>4,8</sup> that its eigenvalues depend only on the total spin  $S$ , on the absolute value  $|\Lambda|$  of the projection of the total electronic orbital momentum  $L$  on the molecular axis,<sup>9</sup> and possibly, for like atoms, on the *gerade* or *ungerade* symmetry of the molecular wave function. In terms of these eigenvalues, which are in general  $R$  dependent, the matrix elements in the  $|jl\rangle$  representation can be obtained by vector coupling techniques.

For definiteness, we restrict our attention to the case where  $L$  and  $S$  can have any value for one of the colliding atoms, while the other one has both  $L=0$  and  $S=0$ , i.e., is in a singlet  $S$  state. Then an expansion basis whose members are eigenfunctions of the projections of  $L$  and  $j$  on the interatomic axis ( $\Lambda$  and  $\Omega$ , respectively)<sup>9</sup> can be chosen. The connection between this  $|\Lambda\Omega\rangle$  representation and the space fixed one can be written as an orthogonal basis transformation

$$|jl\rangle = \sum_{\Lambda\Omega} (-)^{j-\Omega} \langle j\Omega, J-\Omega | l0 \rangle \langle \Lambda\Lambda, S\Sigma | j\Omega \rangle | \Lambda\Omega \rangle \quad (2.3)$$

where  $\langle \dots, \dots | \dots \rangle$  are vector coupling coefficients.<sup>10</sup> Therefore, the matrix elements of the electrostatic interaction for the  $|jl\rangle$  representation are given by

$$V_{j_l, j'_l} = \sum_{\Lambda\Omega\Lambda'\Omega'} (-)^{j-\Omega-\Omega'} \langle j\Omega, J-\Omega | l0 \rangle \langle j'\Omega', J-\Omega' | l'0 \rangle \times \langle \Lambda\Lambda, S\Sigma | j\Omega \rangle \langle \Lambda'\Lambda', S\Sigma' | j'\Omega' \rangle v_{|\Lambda|} \delta_{\Lambda\Lambda'} \quad (2.4)$$

in terms of the eigenvalues  $v_{|\Lambda|}(R)$  of the electrostatic interaction.

Inserting Eq. (2.4) in Eqs. (2.1) and (2.2) leads to the complete specification of the coupled equations. It can be easily verified, by taking  $L=1$  and  $S=\frac{1}{2}$ , that the resulting equations are those derived by Mies<sup>7</sup> for  $H^+-F(^2P)$  collisions, so that his derivation can be taken as a justification of our heuristic procedure, and therefore the validity limits indicated by him also apply here.

The basic point for the following developments is that it is possible to take some advantage from the degree of freedom in the choice of the quantum numbers which characterize the basis. Thus, from an identity in the theory of angular momentum,<sup>10</sup> we can expand the elements of the transformation matrix in Eq. (2.3) as

$$\begin{aligned} & (-)^{j-\Omega} \langle j\Omega, J-\Omega | l0 \rangle \langle \Lambda\Lambda, S\Sigma | j\Omega \rangle \\ &= \sum_K (-)^{j\Omega+K+L-E-\Lambda} [j, K]^{1/2} \left\{ \begin{matrix} S & L & j \\ l & J & K \end{matrix} \right\} \\ & \times \langle \Lambda\Lambda, K-\Lambda | l0 \rangle \langle S-\Sigma, J\Omega | K\Lambda \rangle, \end{aligned} \quad (2.5)$$

where  $\left\{ \begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{smallmatrix} \right\}$  is a 6- $j$  coefficient,<sup>10</sup> and  $[x] \equiv 2x+1$ . Equation (2.5) introduces the quantum number  $K$  of spectroscopy,<sup>4,11</sup> at this stage only as a dummy index. Evidently,

$$K = l + L = J - S; \quad (2.6)$$

we can therefore insert Eq. (2.5) into Eq. (2.4) and perform the summation on  $\Omega$  and  $\Omega'$ , whereby two of the

vector coupling coefficients disappear by orthonormality. The result is an alternative expression for the potential matrix elements

$$V_{j_1, j_1', l} = \sum_{K \Lambda K' \Lambda'} (-)^{j-j'+K-K'+l-l'+\Lambda-\Lambda'} [j, j', K, K']^{1/2} \times \begin{Bmatrix} S & L & j \\ l & J & K \end{Bmatrix} \begin{Bmatrix} S & L & j' \\ l' & J & K' \end{Bmatrix} \times \langle \Lambda K, K - \Lambda | l 0 \rangle \langle \Lambda' K', K' - \Lambda' | l' 0 \rangle v_{\Lambda \Lambda'} \delta_{\Lambda \Lambda'}, \quad (2.7)$$

where now another basis, which we denote by  $|\Lambda K\rangle$ , has been defined by the transformation

$$|\Lambda K\rangle = \sum_{j l} (-)^{j+K+l+S+\Lambda} [j, K]^{1/2} \times \begin{Bmatrix} S & L & j \\ l & J & K \end{Bmatrix} \langle \Lambda K, K - \Lambda | l 0 \rangle |j l\rangle. \quad (2.8)$$

From Eqs. (2.3), (2.5), and (2.8) is immediately found that the orthogonal transformation which relates the bases  $|\Lambda K\rangle$  and  $|\Lambda \Omega\rangle$  is

$$|\Lambda K\rangle = \sum_{\Omega} (-)^{S+\Omega} \langle S - \Sigma, J \Omega | K \Lambda \rangle |\Lambda \Omega\rangle. \quad (2.9)$$

A different approach, which has the virtue of bearing out the connection between the present problem and the well-known close coupling approach to the scattering of a particle by a rigid rotor, has been introduced by Reid and Dalgarno.<sup>6,12</sup> They define an operator for the anisotropic electrostatic interaction and obtain for the matrix elements in the  $|j l\rangle$  representation

$$V_{j l, j' l'} = \sum_{\mu} (-)^{j-S+l-l'} \frac{[L]}{[\mu]} [j, j', l, l']^{1/2} \begin{Bmatrix} j & j' & \mu \\ l' & l & J \end{Bmatrix} \begin{Bmatrix} j & j' & \mu \\ L & L & S \end{Bmatrix} \times \langle L 0, L 0 | \mu 0 \rangle \langle l 0, l' 0 | \mu 0 \rangle v_{\mu}, \quad (2.10)$$

where  $v_{\mu}(R)$  are the coefficients of a Legendre expansion. The relationship between these coefficients and the eigenvalues of the matrix of the electrostatic interaction  $v_{\Lambda \Lambda'}$  can be established by realizing that the matrix whose elements are given by Eq. (2.10) can be diagonalized by the same orthogonal matrix which relates the  $|j l\rangle$  and  $|\Lambda \Omega\rangle$  bases, and whose elements are given by Eq. (2.3). The matrix which relates the  $|j l\rangle$  and  $|\Lambda K\rangle$  bases, whose elements are given by Eq. (2.8), may be used as well for the same purpose. After some angular momentum algebra, one obtains that, in order for the two approaches to coincide, the following identification must be made:

$$v_{\Lambda} = \sum_{\mu} \langle L 0, \mu 0 | L 0 \rangle \langle \Lambda \Lambda, \mu 0 | \Lambda \Lambda \rangle v_{\mu}, \quad (2.11)$$

where the right-hand side is an eigenvalue of the Reid-Dalgarno matrix (2.10). Using the properties of vector coupling coefficients, it is possible to invert the linear system (2.11), and the result is

$$v_{\mu} = \sum_{\Lambda} \frac{[\mu] \langle \Lambda \Lambda, \mu 0 | \Lambda \Lambda \rangle}{[L] \langle L 0, \mu 0 | L 0 \rangle} v_{\Lambda}. \quad (2.12)$$

Explicitly, for  $L = 1$ , the only nonzero terms are

$$v_{\Sigma} = v_0 + (2/5)v_2, \quad v_{\Pi} = v_0 - (1/5)v_2 \quad (2.13)$$

or

$$v_0 = (1/3)v_{\Sigma} + (2/3)v_{\Pi}, \quad v_2 = (5/3)(v_{\Sigma} - v_{\Pi}), \quad (2.14)$$

while, for  $L = 2$ , they are

$$\begin{aligned} v_{\Sigma} &= v_0 + (2/7)v_2 + (2/7)v_4, \\ v_{\Pi} &= v_0 + (1/7)v_2 - (4/21)v_4, \\ v_{\Delta} &= v_0 - (2/7)v_2 + (1/21)v_4, \end{aligned} \quad (2.15)$$

or

$$\begin{aligned} v_0 &= (1/5)(v_2 + 2v_{\Pi} + 2v_{\Delta}), \\ v_2 &= (v_{\Sigma} - v_{\Delta}) + (v_{\Pi} - v_{\Delta}), \\ v_4 &= (9/5)(v_{\Sigma} - v_{\Pi}) + (3/5)(v_{\Delta} - v_{\Pi}), \end{aligned} \quad (2.16)$$

where, as usual,  $\Sigma$ ,  $\Pi$ , and  $\Delta$  stand for  $|\Lambda| = 0, 1$ , and  $2$ , respectively. This formulation is particularly attractive, since the matrix for the  $v_0$  term is a multiple of the unit matrix, and therefore it is unaffected by unitary transformations: It clearly plays the role of an average spherical potential. The anisotropy and therefore the electrostatic coupling for Eq. (2.1) are contained only in the higher terms, in particular only in the  $v_2$  term for  $P$  atoms.

### III. THE FIVE COUPLING CASES

The discussion of the coupled equations in the previous section leads quite naturally to the development of alternative formulations for Eq. (2.1), and to the explicit expressions for the orthogonal matrices which relate them. Although these alternative formulations are actually the result of different choices for the expansion basis of the total scattering wave function, we omit any explicit reference to it, but refer directly to the effect of the transformations on the coupled equations themselves, as written in the matrix form given in Eq. (2.1). Also, since we will end up finding five representations which can be related to the five Hund's cases,<sup>3,4,8</sup> familiar in the spectroscopy of rotating diatomic molecules, we will use, for the designation of the various representations, the parenthesized lower-case letters appropriate to designate the corresponding Hund's cases. Indeed, the space-fixed representation described in the previous section will be designated as follows:

(i) Case (e): In this case, where  $j$  and  $l$  are defined, both the first two terms of Eq. (2.2), representing the spin-orbit and the centrifugal interactions, are diagonal, and the coupling is due only to the electrostatic interaction, whose matrix elements in this representation are given by any of the Eqs. (2.4), (2.7), or (2.10). From the properties of the vector coupling coefficients which appear in these equations, only channels having  $l - l' = 0$  or even are coupled, and therefore the  $V$  matrix factorizes in two blocks: This parity conservation is of course related to the invariance of the interaction with respect to inversion of the space-fixed coordinates. In order to save this factorization as we transform to a body-fixed frame, i.e., move from case (e) to the following:

(ii) Case (c): Here, where  $j$  is still defined but  $l$  is

to be replaced by the projection of  $j$  along the internuclear axis  $\Omega$ , we follow Chang and Fano,<sup>13</sup> who introduce a parity quantum number  $\epsilon$  for a frame transformation in electron-atom collisions. For our purpose, we define  $\epsilon = +1$ , if  $J - l - S$  is zero or even, and  $\epsilon = -1$  otherwise, and by considering the vector coupling sequence displayed in Eq. (2.3) write, for the matrix elements of the (e) - (c) transformation,<sup>14-16</sup>

$$G_{\Omega l}^j = \frac{1 + \epsilon(-)^{J-l-S}}{[2(1 + \delta_{\Omega 0})]^{1/2}} (-)^{J-\Omega} \langle j\Omega, J - \Omega | l0 \rangle. \quad (3.1)$$

It can be shown that, because of the parity factor, this transformation is orthogonal with respect to summation on the allowed  $\Omega \geq 0$ , and on all allowed even (or odd) values of  $l$ . It is also immediately seen from the vector coupling coefficient that it is essentially a frame transformation (where  $\Omega$  plays the role of a helicity<sup>17</sup> quantum number), such as those employed in the theory of scattering by a rigid rotor.<sup>18</sup> As a matter of fact, by operating with Eq. (3.1) on Eq. (2.1) in the (e) case representation, we obtain that in this (c) case, as a typical body-frame situation, the spin-orbit matrix  $\mathcal{E}$  is unaffected by the transformation and so is still diagonal; the centrifugal matrix is no longer diagonal, states with  $\Omega' = \Omega \pm 1$  now being coupled; the electrostatic potential becomes independent of the total angular momentum  $J$ , but is block diagonal with respect to  $\Omega$ . We give only the explicit expression for the latter in the Reid-Dalgarno<sup>6,12</sup> formulation:

$$V_{j\Omega j'\Omega'} = \sum_{\mu} (-)^{2j'-\Omega-S} \frac{[L]}{[\mu]} [j, j']^{1/2} \langle L0, L0 | \mu 0 \rangle \times \langle j\Omega, j' - \Omega | \mu 0 \rangle \begin{Bmatrix} j & j' & \mu \\ L & L & S \end{Bmatrix} \delta_{\Omega\Omega'} v_{\mu}. \quad (3.2)$$

The complete diagonalization of the electrostatic potential matrix leads to (iii)

(iii) Case (a): The transformation from case (c) to case (a), where  $\Omega$  is still defined but  $j$  is replaced by  $\Lambda$ , the projection of  $L$  along the internuclear axis, is effected by a decoupling already manifested in Eq. (2.1): by working out the parity factor, one obtains, for the matrix elements of this orthogonal transformation,<sup>14,15</sup>

$$G_{j\Lambda}^{\Omega} = \left\{ 1 - \delta_{\Omega 0} + \delta_{\Omega 0} \frac{1 + \epsilon(-)^{J-S}}{[2(1 + \delta_{\Omega 0})]^{1/2}} \right\} \langle L\Lambda, S - \Sigma | j\Omega \rangle. \quad (3.3)$$

The results of the application of this transformation are easily seen to be the appearance of off-diagonal terms for the  $\mathcal{E}$  matrix (connecting terms with  $\Lambda' \neq \Lambda$ ) and to the appearance of coupling both for  $\Lambda' \neq \Lambda$  and for  $\Omega' \neq \Omega$  in the centrifugal term. The expression for the matrix elements of the now diagonal electrostatic interaction is given by Eq. (2.11).

The route we have been following from case (e) to (a), through case (c), is seen to correspond to the sequence of coupling schemes exhibited by Eq. (2.3). Alternatively, one may refer to Eq. (2.8), and find first the transformation from case (e) to

(iv) Case (d): In this case,  $l$  is still defined, while  $j$  is replaced by  $K$ . The (e) - (d) transformation is essentially affected by recoupling<sup>14</sup>

$$G_{jK}^l = (-)^{J+K+l+S} [j, K]^{1/2} \begin{Bmatrix} S & L & j \\ l & J & K \end{Bmatrix}. \quad (3.4)$$

when applied to Eq. (2.1), it leaves diagonal the centrifugal potential, introduces couplings in the  $\mathcal{E}$  matrix for states with  $K' \neq K$ , and the electrostatic interaction matrix, whose elements can be shown to be given by

$$V_{lK l'K'} = \sum_{\mu} (-)^{K+l-l'} \frac{[L]}{[\mu]} [l, l']^{1/2} \langle L0, L0 | \mu 0 \rangle \times \langle l0, l'0 | \mu 0 \rangle \begin{Bmatrix} L & L & \mu \\ l' & l & K \end{Bmatrix} \delta_{KK'} v_{\mu}, \quad (3.5)$$

is seen to be block diagonal in  $K$ , but couples states with  $l' \neq l$ . It is interesting to note that in this representation, where  $S$  is decoupled by  $L$ , the  $V$  matrix elements are essentially Percival-Seaton's coefficients<sup>19</sup>: Indeed, the scattering problem resembles the one of a rigid rotor constrained to the rotational quantum number  $L$ , the role of the total angular momentum being played by  $K$ . As suggested by the vector coupling coefficient in Eq. (2.8), the last case which remains to be considered

(v) Case (b): Is obtained by case (d) by means of the space-fixed to body-fixed orthogonal frame transformation<sup>14,15</sup>

$$G_{l\Lambda}^K = \frac{1 + \epsilon(-)^{J-l-S}}{[2(1 + \delta_{\Lambda 0})]^{1/2}} (-)^{L-\Lambda} \langle L\Lambda, K - \Lambda | l0 \rangle. \quad (3.6)$$

In this case,  $K$  is still defined, but  $l$  is replaced by  $\Lambda$ , and the electrostatic interaction matrix is diagonal, its elements being given by Eq. (2.11), as in case (a). Coupling between  $\Lambda' \neq \Lambda$  appears in the centrifugal matrix, while the  $\mathcal{E}$  matrix couples also different  $K$  states.

Finally, the transformation which relates cases (b) and (a) is found to be<sup>14,15</sup>

$$G_{K\Omega}^{\Lambda} = \left\{ 1 - \delta_{\Lambda 0} + \delta_{\Lambda 0} \frac{1 - \epsilon(-)^{J-K-S}}{[2(1 + \delta_{\Omega 0})]^{1/2}} \right\} (-)^{S+\Sigma} \langle S - \Sigma, J\Omega | K\Lambda \rangle \quad (3.7)$$

[compare Eq. (2.9) and, for example, Ref. 20].

The results of this section are summarized graphically in Fig. 1, where the matrix elements for the five transformations are given, omitting for simplicity the parity factors. All the relationships which hold between the various cases can be recovered with the aid of Fig. 1: In particular, it can be verified that each transformation can be expressed by means of the other four, e.g.,

$$G_{jK}^l = \sum_{\Omega \Lambda} G_{l\Lambda}^K G_{K\Omega}^{\Lambda} G_{j\Lambda}^{\Omega} G_{\Omega l}^j, \quad (3.8)$$

and any sequence of two transformations can be expressed as a function of the other three, e.g.,

$$G_{K\Omega}^{\Lambda} G_{j\Lambda}^{\Omega} = \sum_l G_{\Omega l}^j G_{jK}^l G_{l\Lambda}^K.$$

Finally, it can be verified that a complete cycle in any direction, starting from any of the five cases, leads to the unit matrix

$$\sum_{j l K \Lambda \Omega} G_{jK}^l G_{l\Lambda}^K G_{K\Omega}^{\Lambda} G_{j\Lambda}^{\Omega} G_{\Omega l}^j = 1.$$

IV. HIGH  $J$  LIMITS

We consider in this section the simplifying features which emerge in the present approach when the total angular momentum is assumed to be large. This situation is met so often in atomic collisions that the formulas which are obtained have a practical interest. Furthermore, it will be seen that they add insights into the physics by preparing the way towards a semiclassical treatment of the dynamics.

Since  $L$  and  $S$  are fixed, when  $J$  increases, we soon have that, because of the triangular relationships,  $J, l, K \gg L, S, j$ . So in the calculation of the limits as  $J$  goes to infinity in any of the formulas in Sec. III, one is left with vector coupling coefficients in place of the recoupling coefficients which contain large arguments, and with reduced Wigner matrices for a right angle rotation in place of the vector coupling coefficients which contain large angular momenta.<sup>20,21</sup> With the following definitions for differences of angular momenta<sup>22</sup>:

$$\omega = J - l, \quad \lambda = K - l, \quad \sigma = J - K, \quad (4.1)$$

the case designations and the transformation matrix elements displayed in Fig. 2 are obtained, in place of those in Fig. 1. The  $\epsilon$  containing factors, which should appear here as in Fig. 1, are the same as previously, and may be rewritten with the use of Eq. (4.1).

For the electrostatic interaction, only the space-frame representations [cases (e) and (d)] are affected, and Eqs. (2.10) and (3.5) become, respectively, in the high  $J$  limit,

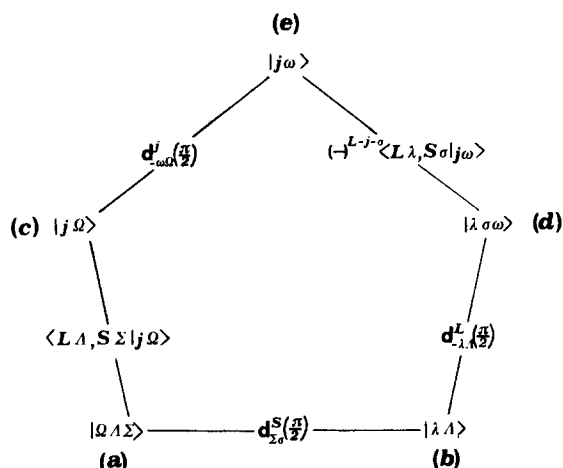


FIG. 2. The limiting form of the diagram in Fig. 1 as  $J \rightarrow \infty$ . The lower-case Greek letters  $\omega$ ,  $\lambda$ , and  $\sigma$  are space-fixed projections of  $j$ ,  $L$ , and  $S$ , respectively, and are related by  $\omega - \lambda - \sigma = 0$ .

$$V_{j\omega j'\omega'} = \sum_{\mu} (-)^{\omega - S - j - j'} \left[ \frac{L}{\mu} \right] [j, j']^{1/2} d_{0\omega' - \omega}^{\mu} \left( \frac{\pi}{2} \right) \begin{Bmatrix} j & j' & \mu \\ L & L & S \end{Bmatrix} \times \langle L0, L0 | \mu 0 \rangle \langle j\omega, j' - \omega' | \mu, \omega - \omega' \rangle v_{\mu}, \quad (4.2)$$

$$V_{\lambda\omega\lambda'\omega'} = \sum_{\mu} (-)^{\lambda - \lambda'} d_{0\lambda' - \lambda}^{\mu} \left( \frac{\pi}{2} \right) \times \langle L0, \mu 0 | L0 \rangle \langle L - \lambda', \mu\lambda' - \lambda | L - \lambda \rangle v_{\mu}. \quad (4.3)$$

The parity selection rule which forbids coupling for odd  $|l - l'|$  values now can be seen to forbid coupling for odd  $|\omega - \omega'|$  values.

The high  $J$  limiting form of the centrifugal potential is also of interest. By first writing

$$l(l+1) \approx [J]^2/4 + [J]\omega \quad (4.4)$$

and then introducing an "impact parameter" by the definition

$$2\mu vb = \hbar[J], \quad (4.5)$$

where  $v = (2E/\mu)^{1/2}$  is an asymptotic velocity depending only on the arbitrary energy scale, one obtains, for the centrifugal potential in the  $|j\omega\rangle$  representation,

$$\frac{\hbar^2 l^2}{2\mu R^2} - E \frac{b^2}{R^2} 1 + \frac{\hbar vb}{R^2} \omega,$$

where  $\omega$  is the diagonal matrix with  $\omega$  as eigenvalues.

Therefore, in the case (e) representation, Eq. (2.1) becomes, for large  $J$  values,

$$\left\{ \left[ \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E \left( 1 - \frac{b^2}{R^2} \right) \right] 1 - \mathcal{E}_j - \frac{\hbar vb}{R^2} \omega - \mathbf{V} \right\} \mathbf{u} = 0, \quad (4.6)$$

where  $\mathcal{E}_j$  and  $\omega$  are diagonal,  $\mathbf{V}$  is given by Eq. (4.2), and the elements of the  $\mathbf{u}$  matrix are labeled by the  $j$  and  $\omega$  quantum numbers. The other representations can be obtained as explained above, and an example will be given in the next section.

Before leaving this section, we must note that Eq. (4.6) and its counterparts in the other representations

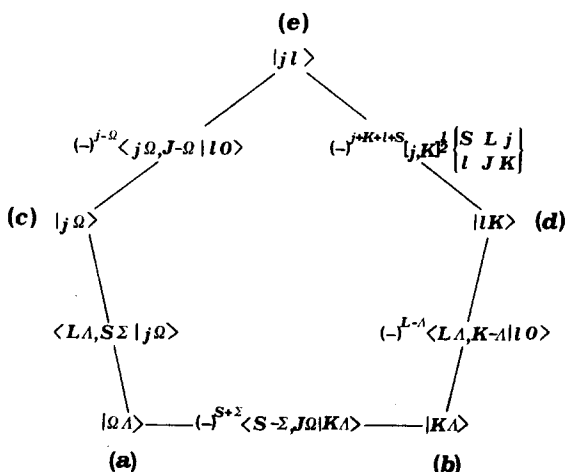


FIG. 1. Diagram showing the connection among the representations corresponding to the five Hund's cases for an atom with inner angular momentum colliding with a  $1S$  species. The orbital angular momentum  $L$  and spin  $S$  of the atom, and the total angular momentum  $J$ , which are constants, are not included in the designation of representations, although they appear in the elements of orthogonal transformations between cases [for the parity depending factors, not included for simplicity, see Eqs. (3.1), (3.3), (3.6), and (3.7)]. The other symbols denote the total atomic angular momentum  $j$  ( $j = L + S$ ), the orbital angular momentum  $l$  ( $l = J - j$ ), and the  $K$  quantum number ( $K = J - S$ );  $\Omega$ ,  $\Lambda$ , and  $\Sigma$  are body-fixed projections of  $j$ ,  $L$ , and  $S$ , respectively, and are related by  $\Omega - \Lambda - \Sigma = 0$ .

are not semiclassical equations, since they are the result of taking the limits of Eq. (2.1) as  $J$  goes to infinity, the dynamics still being treated exactly, i.e., by quantum mechanics. On the other hand, the semiclassical limit requires as a basic step an asymptotic expansion in the inverse of the Planck constant, although the high  $J$  conditions are usually met in practice, and therefore fruitfully exploited.

## V. EXAMPLES

### A. $^1P$ atom + $^1S$ atom

In the almost trivial example that we consider, the collisions of a  $^1P$  atom with a  $^1S_0$  atom, one has  $L=1$  and  $S=0$ , and therefore  $j=j'=1$ , so this index will be dropped from the notation. The coupled equations are a  $3 \times 3$  set, which decouple into a  $1 \times 1$  block for the parity quantum number  $\epsilon=+1$ , and a  $2 \times 2$  block for  $\epsilon=-1$ . We consider for simplicity the high  $J$  limit (4.6) and choose the energy scale so that  $\mathcal{E}_j=0$ . In the (e) representation, for  $\epsilon=+1$ , the equation to be solved for  $u_{\omega\omega'}^+ = u_{00}^+$  is a single channel one, with  $\omega=0$ , and  $V=v_0 - \frac{1}{5}v_2$  in Eq. (4.6): It is obviously unaffected by any change in representation. For  $\epsilon=-1$ , the  $2 \times 2$  matrices<sup>23</sup> in Eq. (4.6) are

$$\omega = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad V \equiv \{V_{\omega\omega'}^-\} = v_0 \mathbf{1} + \frac{v_2}{10} \begin{pmatrix} 1 & -3 \\ -3 & 1 \end{pmatrix} \quad (5.1)$$

and

$$u^- \equiv \{u_{\omega\omega'}^-\} = \begin{pmatrix} u_{11} & u_{1-1} \\ u_{1-1} & u_{-1-1} \end{pmatrix}. \quad (5.2)$$

In this problem, since  $S=0$ , one has  $K=J$ , so the space-fixed representations for cases (e) and (d) coalesce, as can be seen from the degeneration of Eq. (3.4) into a unit matrix. Similarly, since  $\Sigma=0$ , one also has  $\Lambda=\Omega$ , and the body-fixed representations coalesce, so only one alternative for Eqs. (5.1) and (5.2) needs to be considered. Specifically, the elements  $G_{\omega\Omega}$  (dropping unnecessary indexes) of the transformation are found to be

$$G_{10}=G_{11}=-G_{-10}=G_{-11}=(2)^{-1/2},$$

and one obtains

$$\omega \rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \{V_{\Omega\Omega'}^-\} = v_0 \mathbf{1} + \frac{v_2}{5} \begin{pmatrix} 2 & 0 \\ 0 & -1 \end{pmatrix}, \quad (5.3)$$

and

$$\{u_{\Omega\Omega'}^-\} = \begin{pmatrix} u_{00} & u_{01} \\ u_{01} & u_{11} \end{pmatrix}. \quad (5.4)$$

A comparison of Eqs. (5.1) and (5.3) shows that the coupling is transferred by the transformation from the electrostatic term to the centrifugal term. Therefore, as long as  $(\hbar v b/R^2) > (3/10)v_2$ , the set for Eq. (5.2) is more weakly coupled than the set for Eq. (5.4), and the opposite is true for  $(\hbar v b/R^2) < (3/10)v_2$ .

Since in general  $v_2$  is of shorter range than  $\sim R^{-2}$ , the case (e) or (d) representation is better than that for cases (c) or (a) or (b) at large  $R$  values, while the opposite can be true at short ranges.

The picture which emerges for a collision for this system is that of an approximate conservation of the

space-fixed quantum number  $\omega$  or  $\lambda$ , appropriate for the description of separate atoms, until the vicinity of a distance given by  $R = (10\hbar v b/3v_2)^{1/2}$ , where a transition described approximately by a sudden change in coupling scheme leads to a situation for which the molecular quantum number  $\Omega$  or  $\Lambda$  are approximately conserved. The extent that the system penetrates into the inner quasimolecular region depends on the energy, which fixes the classical turning points: The opposite path is followed when the particles separate.

### B. $^2P$ atom + $^1S$ atom

The case of collisions of  $^2P$  atoms with  $^1S_0$  atoms or ions is the more thoroughly investigated: Explicit expressions for the coupled equations, in what we call the case (e) representation, have been given by Reid<sup>6</sup> and Mies.<sup>7</sup> Numerical solutions for these equations for particular systems have been presented by many authors.<sup>8</sup> Also, most of the semiclassical studies have been performed on collisions of  $^2P$  alkali atoms with the rare gases.<sup>3</sup>

Equation (2.1) for this system, where  $L=1$  and  $S=1/2$ , consists of two  $3 \times 3$  blocks, each pertaining to opposite parities. The coupling among states in the case (e) representation is due to the  $v_E - v_N = (3/5)v_2$  term which, being of short range, makes the neglect of coupling in this representation, or its treatment as a small perturbation, particularly useful at long range. When the colliding partners approach, however, the anisotropy in the electrostatic interaction can overcome either the spin-orbit separation in the isolated  $^2P$  atom as measured by its fine structure splitting, or the centrifugal coupling terms, which vary with distance as  $\sim R^{-2}$ . The two alternatives evidently occur for small or large values of the total angular momentum  $J$ , respectively.

The first alternative, when rotation effects dominate over the spin-orbit ones, leads to case (d) as the preferred coupling scheme. A further approach of the atoms, implying the dominance of the electrostatic interaction over the centrifugal one also, would mark the onset of a typical case (b) situation. The collision of the two atoms is being essentially described as giving rise to a quasimolecule, upon which rotation and spin-orbit, in this order of importance, act as perturbations.

The other route which a typical collision may follow at relatively small angular momenta would be, through a case (c) situation, to case (a) and then possibly (b). How close to the molecular cases each collision will go depends essentially on energy, which fixes the classical turning points, and actually the same sequence of coupling situation in a reverse order will be described by the colliding partners as they move apart after reaching the turning points.<sup>24</sup>

We will discuss in more detail the collisions of  $^2P$  atoms in the following paper,<sup>5</sup> where the bounds of dominance of each coupling scheme will be given explicitly in terms of the relevant interactions. In that paper, we will also develop decoupling approximations which this approach suggests, and present numerical

model computations and comparisons with "exact" solutions.

### C. $^3P$ atom + $^1S$ atom

Collisions of a  $^3P$  atom with a  $^1S_0$  species are described by a  $9 \times 9$  Hamiltonian matrix, which decouples by parity into two blocks, having dimensionalities  $4 \times 4$  ( $\epsilon = +1$ ) and  $5 \times 5$  ( $\epsilon = -1$ ): Explicit expressions for the coupled equations in the five representations can be obtained by the formulas in Sec. II by taking  $L = 1$  and  $S = 1$ .

Apart from some semiclassical approaches,<sup>25</sup> this problem appears not to have received much attention, although experiments<sup>1</sup> on elastic scattering of the  $^3P$  metastables of the rare gases and of mercury have been carried out. In connection with experiments performed in this laboratory on integral elastic cross sections of  $O(^3P)$  atoms,<sup>26</sup> we are investigating this problem and developing a program for the exact and approximate solution of the coupled equations. We anticipate that, since for this more complicated problem the physical description given in the previous section for the  $^2P$  collisions can be formulated in exactly the same way, the present approach has been very useful to disentangle some subtle effects observed experimentally.

## VI. EXTENSIONS AND APPLICATIONS

The five alternative representations described in the previous sections. Although worked out for the problem of an atom possessing fine structure with a structureless particle, can be extended in a straightforward manner to the general case in which the inner angular momenta of the second atom have to be taken explicitly into account.<sup>27</sup> The matrix elements can be constructed by suitably extending the structure of the electrostatic operator, e.g., in analogy with the rotor-rotor problem,<sup>28</sup> or by starting directly from the eigenvalues of this operator. These eigenvalues will now depend not only on  $\Lambda$  but also on total spin, and possibly, for like atoms, on *gerade* and *ungerade* symmetry.

While the transformations explicitly given in Sec. III would still apply to modify the coupling schemes for the angular momenta of each atom, similar transformations leading to alternative coupling schemes between the internal angular momenta of the two atoms and those of the relative motion can be found. As a matter of fact, even when the expansion of the total wave function in the components of the atomic fine structure is only a part of a larger basis which includes other states of the atomic manifold, these transformations will lead to equivalent representations, each one showing definite advantages in particular situations.

In conclusion, we summarize a few aspects which characterize this approach. If the close coupling equations are to be solved exactly by numerical methods, then the choice of the proper representation, which at given  $R$  values has smaller coupling terms, could save computing times by allowing larger grids in the propagation of the radial wave function matrix, although perhaps at the expense of complications in the programming

A definite advantage both in simplifying the programming and in saving computing times is in general achieved by working in the case (c) or (d) representations. In fact, in these two representations, the Hamiltonian matrix has some elements which are zero, and their relative number with respect to the nonzero ones increases with the dimension of the problem. For example, in the (c) case representation, matrix elements between channels with  $j' \neq j$  and  $\Omega' \neq \Omega$ ,  $\Omega \pm 1$  are zero: This leads to two zero matrix elements in the  $3 \times 3$  problems for  $^2P$  atom collisions, and to six and 12 zero matrix elements in the  $4 \times 4$  and  $5 \times 5$  problems for  $^3P$  atom collisions. Similar reductions in the number of nonzero elements occur for the case (d) representations: Since they imply simplifications in the programming of matrix manipulations, and an increase in the speed needed for their calculations, representations in case (c) and (d) have advantages over those in the other cases when the set of second order radial Schrödinger equations are being solved exactly. Of course, the same reductions occur when the set of differential equations to be solved is of the first order, as in the impact parameter approximation, or other variants of the semiclassical type.

However, apart from advantages for the exact solution, which are a consequence of the purely formal structure of the problem, it appears that this approach finds its most interesting applications as a guide for finding out approximation schemes, and for its ability of adding insight into the analysis of experimental results. The aspect related to the development of reliable approximation schemes within this context will be dealt with in the accompanying paper,<sup>5</sup> where numerical studies will be presented, particular attention being devoted to the partial or full decoupling of the equations as a consequence of the approximate conservation of specified quantum numbers. Finally, an example of application of the same physical ideas underlying this approach to the interpretation of experimental results will be found in a forthcoming paper,<sup>26</sup> which reports a molecular beam study of the scattering by rare gases of partially polarized  $O(^3P)$  atoms.

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<sup>1</sup>For a review covering work done until 1974, see U. Buck, Adv. Chem. Phys. 30, 313 (1975); more recent papers include the following: on  $O(^3P)$  + rare gases, V. Aquilanti, G. Liuti, F. Pirani, F. Vecchiocattivi, and G. G. Volpi, J. Chem. Phys. 65, 4751 (1976); on  $F(^2P)$  + rare gases, C. H. Becker, P. Casavecchia, and Y. T. Lee, *ibid.* 69, 2377 (1978); 70, 2986 (1979); on  $Cl(^2P)$  + rare gases, C. H. Becker, J. J. Valentini, P. Casavecchia, S. J. Sibener, and Y. T. Lee, Chem. Phys. Lett. 61, 1 (1979); on  $Na(^2P_{3/2})$  + Hg, R. Dürren and H.-O. Hoppe, J. Phys. B 11, 2143 (1978).



- <sup>2</sup>R. W. Anderson, T. P. Goddard, C. Parravano, and J. Warner, *J. Chem. Phys.* **64**, 4037 (1976); W. D. Phillips, G. L. Glaser, and D. Kleppner, *Phys. Rev. Lett.* **38**, 1018 (1977).
- <sup>3</sup>For reviews, see E. E. Nikitin, in *Atomic Physics 4*, edited by G. zu Putlitz, E. W. Weber, and A. Winnacker (Plenum, New York, 1975); E. E. Nikitin and B. M. Smirnov, *Usp. Fiz. Nauk* **124**, 201 (1978) [English translation: *Sov. Phys. Usp.* **21**, 95 (1978)]; see also F. Masnou-Seeuws and R. McCarroll, *J. Phys. B* **7**, 2230 (1974); C. Harel, V. Lopez, R. McCarroll, A. Riera, and P. Wahnon, *ibid.* **11**, 71 (1978).
- <sup>4</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. I Spectra of Diatomic Molecules* (Van Nostrand Company, Princeton, 1950); J. T. Hougen, "The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules, Natl. Bur. Stand. Monogr. **115** (1970).
- <sup>5</sup>V. Aquilanti, P. Casavecchia, G. Grossi, and A. Laganà, *J. Chem. Phys.* **73**, 1173 (1980), following paper.
- <sup>6</sup>R. H. G. Reid, *J. Phys. B* **6**, 2018 (1973).
- <sup>7</sup>F. H. Mies, *Phys. Rev. A* **7**, 942, 957 (1973).
- <sup>8</sup>L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Pergamon, Oxford, 1965); S. Ya. Umanskij and E. E. Nikitin, *Theor. Chim. Acta* **13**, 91 (1969).
- <sup>9</sup>In this section, the projection quantum numbers  $\Lambda$  and  $\Omega$  are considered to be signed quantities, and  $\Sigma = -\Lambda + \Omega$ .
- <sup>10</sup>D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon Press, Oxford, 1968), 2nd edition; A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1960); U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1959); our convention for rotation matrices is as in M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
- <sup>11</sup>The  $K$  quantum number is often denoted by  $N$  in spectroscopy.
- <sup>12</sup>R. H. G. Reid and A. Dalgarno, *Phys. Rev. Lett.* **22**, 1029 (1969).
- <sup>13</sup>E. S. Chang and U. Fano, *Phys. Rev. A* **6**, 173 (1972). Note that while the eigenvalues of the parity operator change sign within each set going from one  $J$  value to its neighbor, according to the present definition, the parity quantum number  $\epsilon$  remains the same for all  $J$  within each set.
- <sup>14</sup>Quantum numbers shown as lower indices are those with respect to which the transformation is orthogonal. The upper index is the quantum number preserved by the transformation. Those quantum numbers, which are good for the whole collision ( $J$ ,  $S$ ,  $L$ , and  $\epsilon$ ), are omitted from the notation.
- <sup>15</sup>Having introduced parity, now the body-fixed projections  $\Lambda$  and  $\Omega$  are restricted to be nonnegative, in agreement with spectroscopic conventions.
- <sup>16</sup>An essentially equivalent transformation has been derived by J. M. Launay, *J. Phys. B* **10**, 3665 (1977).
- <sup>17</sup>M. Jacob and G. C. Wick, *Ann. Phys. (N.Y.)* **7**, 404 (1959); H. Klar, *Nuovo Cimento A* **4**, 529 (1971).
- <sup>18</sup>R. T. Pack, *J. Chem. Phys.* **60**, 633 (1974).
- <sup>19</sup>A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. (London) Ser. A* **256**, 540 (1960); for a recent review, see A. S. Dickinson, *Comp. Phys. Commun.* **17**, 51 (1979).
- <sup>20</sup>K. Alder, A. Bohr, T. Huns, B. Mottelson, and A. Winther, *Rev. Mod. Phys.* **28**, 432 (1956), Eqs. (IIB. 101) and (IIB. 104).
- <sup>21</sup>P. J. Brussaard and H. A. Tolhoek, *Physica (Utrecht)* **23**, 955 (1958); G. Ponzano and T. Regge, in *Spectroscopy and Group Theoretical Methods in Physics* (North-Holland, Amsterdam, 1968); K. Schulten and R. G. Gordon, *J. Math. Phys.* **16**, 1971 (1975).
- <sup>22</sup>The use in the notations of lower case Greek letters is introduced to suggest (see Fig. 2) that these quantities are the counterparts of the body-fixed projections  $\Omega$ ,  $\Lambda$ , and  $\Sigma$ , i.e., that they play the role of space-fixed projections of  $j$ ,  $L$ , and  $S$ .
- <sup>23</sup>The trivial reduction in the dimension of the sets, which occurs for  $J < j$ , is of no practical interest.
- <sup>24</sup>Actually, in all cases known to us, the anisotropy term  $v_2$  changes sign at some interatomic distance. However, this usually occurs at distances so large that this feature has no effect on the dynamics.
- <sup>25</sup>A. I. Voronin and V. A. Kvilidze, *Theor. Chim. Acta* **8**, 334 (1967); M. A. D. Fluendy, J. H. Kerr, and K. P. Lawley, *Mol. Phys.* **28**, 69 (1974).
- <sup>26</sup>V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, *J. Chem. Phys.* **73**, 1181 (1980).
- <sup>27</sup>D. C. S. Allison and P. G. Burke, *J. Phys. B* **2**, 941 (1969); J. C. Weisheit and N. F. Lane, *Phys. Rev. A* **4**, 171 (1971); A. W. Yau and A. Dalgarno, *Astrophys. J.* **206**, 652 (1976); J. M. Launay and E. Roueff, *Astron. Astrophys.* **56**, 289 (1977).
- <sup>28</sup>See, for example, A. E. DePristo and M. H. Alexander, *J. Chem. Phys.* **66**, 1234 (1977).