

Theory of Long-Range Interatomic Forces. II. First-Order Interaction Energies in the Uncoupled Representation*

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General methods are developed to calculate the matrix elements between two arbitrary states and for any multipole order. The results are expressed in terms of generalized hypergeometric functions. Some delta conditions in the formula for the electrostatic potential allow substantial factorization of the secular determinant. A device called the interaction diagram is introduced to facilitate the ordering of the secular determinant and the classification of the resulting molecular states. The theory is first applied to systems in which spin-orbit effects are neglected. The energy curves between an alkali atom in the ground state and an alkali

atom in the first and second excited states, two alkali atoms in the first excited state, and an alkali atom in the first and another in the second excited state are calculated. In the last case, where some matrix elements consist of more than one multipole term, the competition of multipoles leads to energy curves which have maxima and minima in first order. It is also shown that for the interaction between atoms in excited states the resonance forces are less dominant while configuration interactions and the forces obtained from simple product state functions become more and more important.

I. INTRODUCTION

IN the calculation of the long-range interaction energies between atoms in nondegenerate S states¹ there was no need to calculate the general first order off-diagonal matrix element since the approximate second-order formula of I-22² required only the knowledge of one diagonal matrix element. If, on the other hand, we are dealing with atoms which are excited or which are in degenerate ground states, then the first-order matrix elements generally do not vanish, and a more general formalism is needed. Here again we perform a perturbation calculation assuming that the unperturbed eigenvalue problem has been solved. We then inquire to what extent the long-range interaction energies are affected when we change the internal structure of one or both atoms. One such change which we shall consider in this paper is the excitation of the atoms. Another one is the effect of spin-orbit coupling which will be treated in paper III of this series.

The theory of long-range interactions between atoms in excited states differs in a number of ways from that presented in I. At large internuclear separations the first order interactions dominate over the second order dispersion forces, and configuration interactions result in a number of distinct energy curves. In addition, if the two atoms have a high enough excitation, the interaction energy receives contributions from more than one multipole. These multipoles very often compete, resulting in pronounced maxima and minima which are entirely electrostatic in nature.

Even for low excited states the secular determinants become prohibitively large and the rearranging of the primitive functions to factorize the determinant and to form molecular subdeterminants is a tremendous task. In order to avoid this we shall introduce a device called

the interaction diagram which will allow us to find immediately the number and size of the possible subdeterminants.

Our aim is to find general methods to calculate the first order matrix elements, to factorize the secular determinants as much as possible, and to show the importance of the different effects on some specific examples.

II. FIRST-ORDER ELECTROSTATIC MATRIX ELEMENTS

Since it is our purpose to develop a rather embracing theory of the interaction between atoms in excited states, we shall first calculate the general matrix element between two arbitrary states of the system for an arbitrary multipole interaction. For the factors of the matrix element which involve angles, the use of the theory of angular momentum yields a closed form; for the radial parts, however, the situation is more complicated since we have to perform an integration over products of Laguerre polynomials with arbitrary arguments and indices.

The form of (I-1) for the electrostatic energy permits the factorization of the first order matrix elements in the following way:

$$\begin{aligned} \langle p' | V | p \rangle = & \sum_{a,b} \sum_{\alpha,\beta} \frac{16\pi^2 e^2}{(2a+1) [(2b+1)!!]} \mathcal{Y}_{b\beta}(\nabla) \Upsilon_a^\alpha(\mathbf{R}) \\ & \times (q_1' | Y_{a\alpha}^*(\theta_1, \varphi_1) | q_1) (q_2' | Y_{b\beta}^*(\theta_2, \varphi_2) | q_2) \\ & \times \langle n_1' l_1' | r_1^a | n_1 l_1 \rangle \langle n_2' l_2' | r_2^b | n_2 l_2 \rangle, \quad (1) \end{aligned}$$

where p' and p represent two states of the system, and q stands for l, m . The subscript 1 refers to atom 1, the subscript 2 to atom 2; a and b denote the specific multipole approximation and the summation over α and β arises from the contraction of the irreducible tensors.

If we are using hydrogenic state functions with adjustable screening parameters Z^* , the radial matrix elements of (1) can be easily evaluated for special values

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¹ P. R. Fontana, preceding paper [Phys. Rev. **123**, 1865 (1961)].

² All references to the first paper will be denoted by I.

of n', l' and n, l . Waller³ and Van Vleck⁴ calculated the diagonal matrix elements for all integral values of a from $+2$ to -6 . The general radial matrix element can be evaluated using methods developed by Erdélyi,⁵ Mayr,⁶ and Buchholz.⁷ The details of the calculation are given in the Appendix.

The remaining factors in (1) depend on the spatial orientation of the two charge distributions, and can be calculated using the theory of angular momentum. The following derivations are based on the fact that the spherical harmonics are irreducible tensors.

In the calculation of the interaction energies between alkalis we shall distinguish two cases. In the first, the effect of the spins of the two valence electrons is neglected, whereas in the second, the spin and orbital angular momentum are correctly coupled and the representation is diagonal with respect to the spin-orbit Hamiltonian $H_{1,s}$. It is evident that this coupled representation can be used only so long as the electrostatic interaction V is a true perturbation. In other words, the coupled representation is valid if $V \ll H_{1,s}$.

On the other hand, in the uncoupled representation, the state function of the system consists of simple product state functions. The inclusion of the spin functions does not change the interaction energy since V is spin independent. The degeneracy of each energy curve, however, is four times as great, since the spins of the two valence electrons can combine to yield a singlet and a triplet state.

The coupled representation and the relation between the coupled and uncoupled representation is discussed in paper III where, in addition, the transition region in which $V \cong H_{1,s}$ is investigated.

In the uncoupled representation, the result of the integration over the spherical harmonics can be expressed in terms of the C coefficients. Using the notation of (1) we have from (I-15)

$$\begin{aligned} \langle q' | Y_{a^*}(\theta, \varphi) | q \rangle \\ = \langle l' m' | Y_{a^*}(\theta, \varphi) | l m \rangle \\ = (-)^a \left[\frac{(2l+1)(2a+1)}{4\pi(2l'+1)} \right]^{\frac{1}{2}} C(l a l'; m, -\alpha, m') \\ \times C(l a l'; 000). \quad (2) \end{aligned}$$

If we substitute (2) into (1) we see that the total matrix element becomes proportional to $C(l_1 a l'_1; m_1, -\alpha, m'_1) C(l_2 b l'_2; m_2, -\beta, m'_2)$. These C coefficients, however, are zero unless the following conditions are satisfied:

$$m_1 - \alpha = m'_1; \quad m_2 - \beta = m'_2. \quad (3)$$

³ I. Waller, *Z. Physik* **38**, 635 (1926).

⁴ J. H. Van Vleck, *Proc. Roy. Soc. (London)* **A143**, 679 (1934).

⁵ A. Erdélyi, *Math. Z.* **40**, 693 (1936).

⁶ K. Mayr, *Math. Z.* **39**, 597 (1935).

⁷ H. Buchholz, *Die Konfluente Hypergeometrische Funktion* (Springer-Verlag, Berlin, 1953), pp. 135-144.

As long as we do not specify the direction of \mathbf{R} with respect to the two coordinate systems, the above relations are two separate conditions. If, however, we let \mathbf{R} coincide with the positive Z axis, we have from (I-5) the additional condition: $\alpha = -\beta$. Combining the three relations yields

$$m_1 + m_2 = m'_1 + m'_2, \quad (4)$$

which indicates that only states with the same total M can combine. This procedure factors the secular determinant into subdeterminants which can be classified by the molecular designation Λ .

III. FACTORIZATION OF THE SECULAR DETERMINANT

In the calculation of first-order interaction energies between atoms in excited states, the main difficulty arises in the reduction of the secular determinant. The energy levels obtained from the use of hydrogen-like state functions are degenerate with respect to l and m , and even low excited states yield very large secular determinants. The application of group theory makes it possible to factorize the determinants. One method has already been outlined in the previous section where it has been shown that suitable rotation of the coordinate systems produces quantization about the internuclear axis, and causes all matrix elements to vanish except those which have the same total M . In the case of the uncoupled representation, where the unperturbed state is $(n_1 n_2)^2$ -fold degenerate, the number of separate subdeterminants is $2n_1 + 2n_2 - 3$. One can show that these representations are completely reducible; i.e., the secular determinant can be diagonalized. Due to the limited number of symmetry conditions, it is not possible to achieve this reduction completely; the remaining subdeterminants have to be solved in order to find the new eigenvalues and eigenfunctions.

The exact root of the remaining subdeterminants tends to mix the states. In many cases, the comparison of the diagonal matrix element with the exact solution shows that the configuration interaction not only changes the internuclear dependence of the energy curve but also its sign. We shall show that this "mixing" is especially strong for Σ states.

If the two interacting alkalis are identical, then an additional symmetry operation can be used to reduce the secular determinants. The identity of the two atoms implies that quantum mechanically we cannot specify the individual states if the two states can be connected in the spectroscopic sense. Here we have to write the unperturbed state function of the system as follows

$$\psi = \frac{1}{\sqrt{2}} [\psi_{\xi}(\text{I})\psi_{\eta}(\text{II}) + \sigma\psi_{\eta}(\text{I})\psi_{\xi}(\text{II})], \quad (5)$$

where ξ and η denote the two states, and σ can take on the values $+1$ or -1 . This resonance effect introduces multipoles of low order in the interaction energy, thus

appreciably changing the long-range behavior of the energy curves.

For the calculation of the interaction energy between alkalis in excited states, we again shall use hydrogen-like state functions with adjustable effective nuclear charges Z^* . As mentioned in I, Z^* is determined from the energy spectrum of the separated atoms. Some care has to be taken in the application of this method. It is not expected that Z^* should remain constant at very small internuclear separations where the charge distributions overlap appreciably. Indeed, several authors⁸ have shown that the effective nuclear charge may vary considerably in these regions. Hirschfelder and Linnett,⁹ however, proved that in the case of H_2 the nuclear charge is approximately unity for $R > 3a_0$. Actually, even at very large separations, Z^* is slightly less than one and it is assumed that the difference arises from the mutual Van der Waals polarization of the two atoms.

If it were possible to remove all degeneracies of the system before the perturbation V is applied, then the secular determinants would be diagonal to begin with, and the problem of factorization would not occur. This primary removal of the degeneracies can often be partially achieved by considering coupled representations. We shall show that the order of the sub-determinants is considerably smaller if the electrostatic perturbation is applied to a system which includes the spin-orbit coupling correctly than to one for which the spin effects are neglected. This method, however, is only applicable as long as $V \ll H_{1,s}$ and thus cannot be used at very small internuclear separations.

As shown in the previous section, a suitable rotation of the coordinate systems quantizes the total angular momentum of the system along the internuclear axis, and the determinant $|A|$ in the equation

$$|A - 1E| = 0, \quad (6)$$

factors as follows

$$|A| = \begin{vmatrix} \Delta_+ & & & & \\ & \Pi_+ & & & \\ & & \Sigma & & \\ & & & \Pi_- & \\ & & & & \Delta_- \end{vmatrix}. \quad (7)$$

The unit matrix in (6) occurs because all state functions used here belong to orthonormal sets. The determinant $|A|$ extends over a particular degenerate state of the system, and its order is $(n_1 n_2)^2$. The $2n_1 + 2n_2 - 3$ sub-

⁸ H. J. Kopineck, Z. Naturforsch. **7a**, 22, 314 (1952). M. Wolfsberg, J. Chem. Phys. **21**, 2166 (1953).

⁹ J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. **18**, 130 (1950).

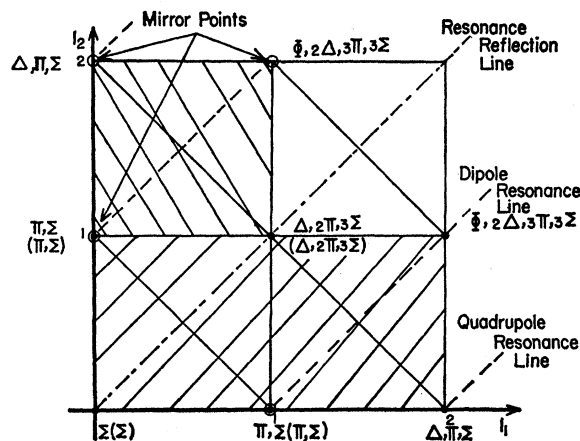


FIG. 1. Interaction diagram of an alkali atom in the first excited state and an alkali atom in the second excited state.

determinants in (7) are distinguished by the molecular designation $\Lambda = \Sigma, \Pi_{\pm}, \Delta_{\pm}$ etc. which correspond to $M_L = 0, \pm 1, \pm 2$. One can show by considering the characters of the representation that the eigenvalues obtained from the Δ_+ subdeterminants are equal to the ones of the Δ_- . Thus the electrostatic perturbation does not produce any Λ -type doubling, and in the following we shall omit the subscripts $+$ and $-$.

In the following applications, the resulting energy curves are distinguished by the molecular term symbol, and in brackets we shall also give the orbital configuration of the unperturbed states. It will turn out that many states are hybrids, and there the complete orbital configuration cannot be given. Since we are dealing here with hydrogen-like atoms, we can also assign a total spin to each function. At large internuclear separations, however, the singlet and triplet curves are degenerate, and the notation is only useful at small separations where the exchange forces remove the degeneracy.

An examination of the secular determinant shows that a device which we call the interaction diagram is a very convenient tool for analyzing the interactions. It permits the determination of many properties of the resulting molecular energy curves without calculation, and it also facilitates greatly the classification of the states.

In order to explain the features of the interaction diagram more clearly, let us consider as an example the interaction between an alkali atom in the first excited state and another one in the second excited state. The corresponding interaction diagram is given in Fig. 1.

The following general rules apply to the interaction diagram:

1. Each point having integral coordinates represents a certain state or states of the system.
2. The units of length on the axis l_1 and l_2 depend on the two interacting atoms.
3. The area bounded by a line connecting all points

which belong to the same degenerate set is called the configuration area.

4. A number of molecular term symbols can be assigned to each point. The point (i, j) where i and j stand for the coordinates of the point in $l_1 l_2$ space represents $i+j+1$ different molecular states. For $\Lambda = i+j-k$ there are $k+1$ such states provided $k \leq 2i$ or $2j$, whichever is smaller, and for $\Lambda \leq j-i$ or $i-j$ the number of molecular states is $2i+1$ or $2j+1$, respectively ($\Lambda \geq 0$; $i, j, k = \text{integers}$).

5. A point on a resonance line can exhibit that specific resonance, and the resulting mirror point will also belong to the configuration area, provided the units of the two axes are the same. In the calculation of the allowed multipoles and matrix elements, the point (i, j) is connected with its mirror image (j, i) . However, no new states are formed when a mirror point coincides with a regular point.

6. The total number of molecular states and the order of each molecular subdeterminant can be obtained by adding up all the term symbols of the points belonging to the configuration area.

7. The possible multipoles connecting point (i, j) and (k, l) can be written in the form $(i+k-2m) - (j+l-2n)$; $m, n = 0, 1, 2, \dots$ where the number in the two brackets determine the two multipoles. This result can also be obtained graphically from the diagram. For instance, the point $(0, 1)$ can be connected with point $(1, 1)$ with a dipole-quadrupole moment. From this result we see that two points on one of the main axes cannot combine.

All these rules can be easily proved by considering the degeneracies of the unperturbed state functions and by remembering that the possible multipoles in the matrix element $\langle \psi' | V | \psi \rangle$ are determined by the parity coefficients $C(l'_1 a l_1; 000)$ and $C(l'_2 b l_2; 000)$ which vanish unless $a = l'_1 + l_1, l'_1 + l_1 - 2, \dots$ and $b = l'_2 + l_2, l'_2 + l_2 - 2, \dots$, respectively. In the case of two identical atoms the resonance contributions are proportional to $C(l'_2 a l_1; 000)C(l'_1 b l_2; 000)$ and this product vanishes unless the conditions $a = l'_2 + l_1, l'_2 + l_1 - 2, \dots$ and $b = l'_1 + l_2, l'_1 + l_2 - 2, \dots$ are satisfied.

Thus by using the interaction diagram we can obtain the conditions for resonance, the number and order of the molecular subdeterminants, the number of nondegenerate energy curves and their general internuclear dependence, the extent of configuration interactions, and the possible multipoles in the secular determinant.

If we apply all these rules to Fig. 1, we see that there are $1\Phi, 4\Delta, 8\Pi$, and 10Σ states if resonance cannot exist, and $2\Phi, 7\Delta, 12\Pi$, and 14Σ states if resonance is possible. We can also immediately conclude that without resonance the Φ state interaction energy is made up of a quadrupole-quadrupole and a quadrupole- 2^4 pole term. The inclusion of resonance splits Φ into a g and a u state and introduces additional dipole-dipole, dipole-octupole, and octupole-octupole terms. The Δ states are much less affected by the configuration interaction than the Σ

states since they do not extend through the whole configuration area. The Σ states, on the other hand, cover the entire configuration area, and it is not surprising that many of them are hybrids.

IV. RESONANCE INTERACTIONS OF NORMAL AND EXCITED ATOMS

As a first application of the theory, let us calculate the interaction energies between an alkali atom in its ground state and another in the first excited state. From the interaction diagram (Fig. 2) we conclude that the first order interaction energy between two dissimilar atoms is zero (the two points on the l_1 axis cannot combine), and that for similar atoms dipole resonance produces two Π states with different symmetries, two Σ states, one of which is a g and the other one a u state, and two degenerate Σ states. The secular determinant is already diagonal and the eigenfunctions are obtained from (5).

The different energy curves are distinguished by the molecular term symbols and the orbital configuration of the separate atoms. Each of these curves corresponds to a singlet and a triplet state of the molecular system. For completeness the term symbols of these are also given in curly brackets. The results are:

$$\Pi_g(1S, 2P_1) = \frac{-C}{3Z_1^* Z_2^* R^3}, \quad \{^1\Pi_g, ^3\Pi_u\} \quad (8)$$

$$\Pi_u(1S, 2P_1) = \frac{C}{3Z_1^* Z_2^* R^3}, \quad \{^1\Pi_u, ^3\Pi_g\} \quad (9)$$

$$\Sigma^+(1S, 2S) = 0,$$

$$\Sigma_g^+(1S, 2P_0) = \frac{2C}{3Z_1^* Z_2^* R^3}, \quad \{^1\Sigma_g^+, ^3\Sigma_u^+\} \quad (10)$$

$$\Sigma_u^+(1S, 2P_0) = \frac{-2C}{3Z_1^* Z_2^* R^3}, \quad \{^1\Sigma_u^+, ^3\Sigma_g^+\}$$

where $C = 32\,768/19\,683$. Z_1^* and Z_2^* are, respectively, the effective nuclear charges of the ground state and first excited state of the alkali atoms.

These results agree in the case of H-H with the findings of Mulliken¹⁰ but disagree with the results of King and Van Vleck.¹¹

Secondly let us consider the interaction of an alkali atom in the ground state with another one in the second excited state. The corresponding interaction diagram is given in Fig. 3. As in the last example, only resonance effects introduce nonzero first-order interaction energies. In Fig. 3, the point $(0, 0)$ cannot be connected with any other point of the configuration interaction region, and

¹⁰ R. S. Mulliken, Bull. Am. Phys. Soc. 4, 173 (1959).

¹¹ G. W. King and J. H. Van Vleck, Phys. Rev. 55, 1165 (1939).

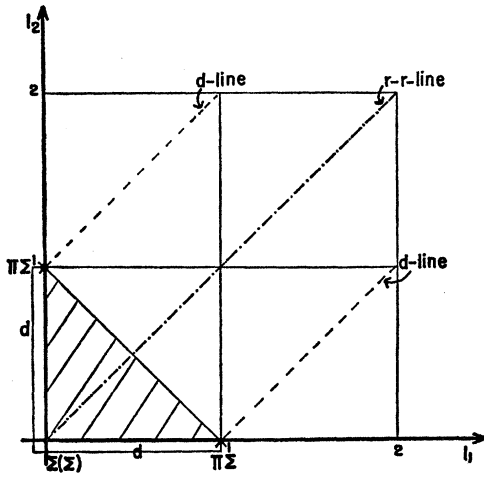


FIG. 2. Interaction diagram of an alkali atom in the ground state and an alkali atom in the first excited state.

consequently these states are diagonal and degenerate. In addition there are one Δ_g , one Δ_u , two Π_g , two Π_u , two Σ_g , and two Σ_u states. The possible multipoles of the diagonal and off-diagonal matrix elements are indicated in the figure.

In the case of the Π and Σ states, the resulting energy curve can always be obtained by solving the remaining 2×2 secular determinants. Very often, however, it is convenient to state the result as a power series of R^{-1} . This can be accomplished by setting

$$E = \frac{\alpha}{R^3} + \frac{\beta}{R^4} + \frac{\gamma}{R^5} + \frac{\delta}{R^6} + \frac{\epsilon}{R^7} + \dots, \quad (11)$$

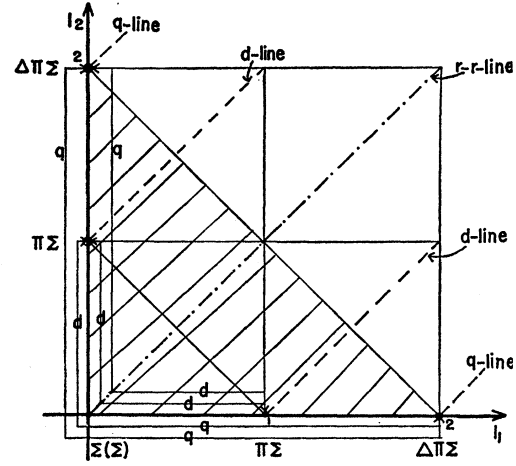


FIG. 3. Interaction diagram of an alkali atom in the ground state and an alkali atom in the second excited state.

and then substituting this expression into the secular determinant. The expansion of the secular determinant leads to a polynomial in the constants, $\alpha, \beta, \gamma, \dots$. These unknowns can be determined by setting the coefficient of a given power of R^{-1} equal to zero and then solving the partially decoupled equations by starting with the one which has been obtained from the lowest power of R^{-1} . These expansions converge very rapidly for $R > 15a_0$. One can also prove that all such series expressing first order interaction energies contain only odd powers of R^{-1} . In many cases, the error made by using a three term expansion is less than 0.1% for $R > 15a_0$.

The interaction energies between two similar alkali atoms, one of which is in the ground state and the other in the second excited state are given below.

$$\Delta_g(1S, 3D_2) = -\Delta_u(1S, 3D_2) = \frac{19\,683}{32\,768Z_1^{*2}Z_2^{*2}R^5}, \quad (12)$$

$$\{^1\Delta_g, ^3\Delta_u\} \quad \{^1\Delta_u, ^3\Delta_g\}$$

$$\Pi_g(1S, 3D_1) = -\Pi_u(1S, 3D_1) = \frac{\gamma_1}{R^5} + \frac{\epsilon_1}{R^7} + \dots, \quad (13)$$

$$\{^1\Pi_g, ^3\Pi_u\} \quad \{^1\Pi_u, ^3\Pi_g\}$$

with

$$\gamma_1 = \frac{59\,049}{131\,072Z_1^{*2}Z_2^{*3}} - \frac{98\,415}{65\,536Z_1^{*2}Z_2^{*2}} + \frac{59\,049}{131\,072Z_1^{*3}Z_2^{*2}},$$

and

$$\epsilon_1 = \frac{4\,782\,969}{2\,097\,152Z_1^{*2}Z_2^{*5}} - \frac{1\,594\,323}{524\,288Z_1^{*2}Z_2^{*4}} - \frac{11\,160\,261}{1\,048\,576Z_1^{*3}Z_2^{*3}} - \frac{1\,594\,323}{524\,288Z_1^{*4}Z_2^{*2}} + \frac{4\,782\,969}{2\,097\,152Z_1^{*5}Z_2^{*2}},$$

$$\Pi_g(1S, 3P_1) = -\Pi_u(1S, 3P_1) = \frac{\alpha_2}{R^3} + \frac{\gamma_2}{R^5} + \frac{\epsilon_2}{R^7} + \dots, \quad (14)$$

$$\{^1\Pi_g, ^3\Pi_u\} \quad \{^1\Pi_u, ^3\Pi_g\}$$

with

$$\alpha_2 = -\frac{729}{8192Z_1^*Z_2^*},$$

$$\gamma_2 = -\frac{59\,049}{131\,072Z_1^*Z_2^{*3}} - \frac{59\,049}{65\,536Z_1^{*2}Z_2^{*2}} + \frac{59\,049}{131\,072Z_1^{*3}Z_2^*},$$

and $\epsilon_2 = -\epsilon_1$.

$$\Sigma_g^+(1S, 3D_0) = -\Sigma_u^+(1S, 3D_0) = \frac{\gamma_3}{R^5} + \frac{\epsilon_3}{R^7} + \dots, \quad (15)$$

$$\{^1\Sigma_g^+, ^3\Sigma_u^+\} \quad \{^1\Sigma_u^+, ^3\Sigma_g^+\}$$

with

$$\gamma_3 = -\frac{177\,147}{262\,144Z_1^*Z_2^{*3}} + \frac{295\,245}{131\,072Z_1^{*2}Z_2^{*2}} - \frac{177\,147}{262\,144Z_1^{*3}Z_2^*},$$

and

$$\epsilon_3 = \frac{43\,046\,721}{16\,777\,216Z_1^*Z_2^{*5}} - \frac{14\,348\,907}{4\,194\,304Z_1^{*2}Z_2^{*4}} - \frac{100\,442\,349}{8\,388\,608Z_1^{*3}Z_2^{*3}} - \frac{14\,348\,907}{4\,194\,304Z_1^{*4}Z_2^{*2}} + \frac{43\,046\,721}{16\,777\,216Z_1^{*5}Z_2^*}, \quad (16)$$

$$\Sigma_g^+(1S, 3P_0) = -\Sigma_u^+(1S, 3P_0) = \frac{\alpha_4}{R^3} + \frac{\gamma_4}{R^5} + \frac{\epsilon_4}{R^7} + \dots,$$

$$\{^1\Sigma_g^+, ^3\Sigma_u^+\} \quad \{^1\Sigma_u^+, ^3\Sigma_g^+\}$$

with

$$\alpha_4 = \frac{729}{4096Z_1^*Z_2^*},$$

$$\gamma_4 = -\frac{177\,147}{262\,144Z_1^*Z_2^{*3}} + \frac{177\,147}{131\,072Z_1^{*2}Z_2^{*2}} + \frac{177\,147}{262\,144Z_1^{*3}Z_2^*},$$

and $\epsilon_4 = -\epsilon_3$.

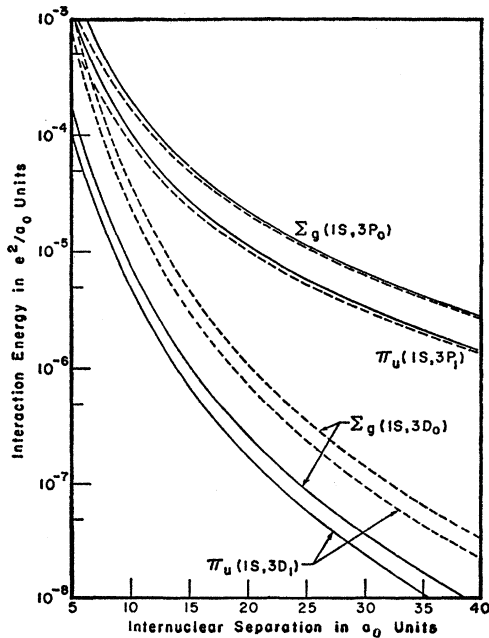


FIG. 4. Repulsive interaction energy curves between a hydrogen atom in the ground state and a hydrogen atom in the second excited state. The dashed curves are obtained from diagonal matrix.

One interesting fact can be noted from these results. In the secular determinant, the highest permissible multipole is a quadrupole-quadrupole term. The first and third term in the γ 's of the Π and Σ states, however, arise from dipole-octupole and octupole-dipole contributions. As a matter of fact, all the multipoles which have the same internuclear dependence are represented in the terms of (13)–(16).

Figure 4 shows the repulsive Π and Σ energy curves for H–H from $R=5a_0$ to $R=40a_0$. The upper two curves are due to dipole resonance and the two lower ones arise from quadrupole resonance. The effect of the configuration interaction can be investigated by com-

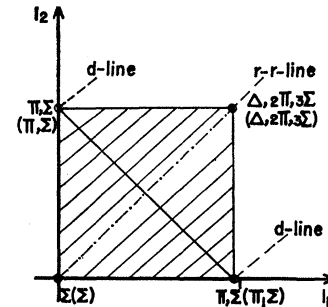


FIG. 5. Interaction diagram of two alkali atoms in the first excited state.

paring the dashed lines which are obtained from the diagonal matrix elements with the full lines. The indicated range does not imply that long-range force calculations are still valid at $R=5a_0$.

V. INTERACTION ENERGIES BETWEEN ATOMS IN EXCITED STATES

So far we have encountered only resonance interactions and the effect of configuration mixing has played a minor role. If both atoms are in excited states, then the first order interaction energies between dissimilar atoms do not vanish and configuration interactions will be quite important. We shall also describe a new effect which can arise only if the system satisfies the condition: $l_1+l_2 \geq 3$. In those cases, the individual matrix elements will contain more than one multipole, and we shall

show that this "competition of multipoles" can lead to maxima and minima in the energy curves.

The interaction between two alkali atoms in first excited states will be treated first. In this case there is no real resonance. From Fig. 5 we note that all the resonance points coincide with regular points, and this implies that the introduction of resonance does not produce new points, and this leaves the configuration area unaltered. In terms of the secular determinant, this means that depending on the approach we group the primitive set of eigenfunctions differently without introducing new states.

In the following results the term symbols apply to the interaction between similar atoms, but the formula also can be used to determine the interaction energy between dissimilar atoms by distinguishing the two effective nuclear charges.

$$\Delta_g(2P_1, 2P_1) = \frac{216}{Z_1^* Z_2^* R^5}, \quad \{^1\Delta_g, ^3\Delta_u\} \quad (17)$$

$$\Pi_u(2P_0, 2P_1) = 0, \quad \{^1\Pi_u, ^3\Pi_g\} \quad (18)$$

$$\Pi_u(2S, 2P_1) = \frac{9}{Z_1^* Z_2^* R^3}, \quad \{^1\Pi_u, ^3\Pi_g\} \quad (19)$$

$$\Pi_g(2P_0, 2P_1) = \left[\frac{324}{Z_1^* Z_2^* R^3} - \frac{216}{Z_1^* Z_2^* R^5} + \frac{324}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^5} - \left[\frac{11\,664}{Z_1^* Z_2^* R^5} + \frac{15\,552}{Z_1^* Z_2^* R^5} \right. \\ \left. + \frac{7776}{Z_1^* Z_2^* R^3} + \frac{15\,552}{Z_1^* Z_2^* R^5} + \frac{11\,664}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^7} + \dots, \quad \{^1\Pi_g, ^3\Pi_u\} \quad (20)$$

$$\Pi_g(2S, 2P_1) = -\frac{9}{Z_1^* Z_2^* R^3} - \left[\frac{324}{Z_1^* Z_2^* R^3} + \frac{648}{Z_1^* Z_2^* R^5} + \frac{324}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^5} \\ + \left[\frac{11\,664}{Z_1^* Z_2^* R^5} + \frac{15\,552}{Z_1^* Z_2^* R^5} + \frac{7776}{Z_1^* Z_2^* R^3} + \frac{15\,552}{Z_1^* Z_2^* R^5} + \frac{11\,664}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^7} + \dots, \quad \{^1\Pi_g, ^3\Pi_u\} \quad (21)$$

$$\Sigma_u^+(2S, 2P_0) = -\frac{18}{Z_1^* Z_2^* R^3}, \quad \{^1\Sigma_u^+, ^3\Sigma_g^+\} \quad (22)$$

$$\Sigma_u^-(2P_1, 2P_{-1}) = 0, \quad \{^1\Sigma_u^-, ^3\Sigma_g^-\} \quad (23)$$

$$\Sigma_g^+(2S, 2S) = 0, \quad \{^1\Sigma_g^+, ^3\Sigma_u^+\} \quad (24)$$

$$\Sigma_g^+(2S, 2P_0) = \frac{18}{Z_1^* Z_2^* R^3} - \left[\frac{972}{Z_1^* Z_2^* R^3} + \frac{1944}{Z_1^* Z_2^* R^5} + \frac{972}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^5} \\ + \left[\frac{262\,440}{Z_1^* Z_2^* R^5} + \frac{1\,189\,728}{Z_1^* Z_2^* R^5} + \frac{1\,854\,576}{Z_1^* Z_2^* R^3} + \frac{1\,189\,728}{Z_1^* Z_2^* R^5} + \frac{262\,440}{Z_1^* Z_2^* R^5} \right] \frac{1}{R^7} + \dots, \quad \{^1\Sigma_g^+, ^3\Sigma_u^+\} \quad (25)$$

$$\begin{aligned}
\Sigma_g^+(2P_0, 2P_0) = & \frac{9\sqrt{6}}{Z_1^* Z_2^* R^3} + \left[\frac{486+243\sqrt{6}}{Z_1^* Z_2^{*3}} + \frac{1620+486\sqrt{6}}{Z_1^{*2} Z_2^{*2}} + \frac{486+243\sqrt{6}}{Z_1^{*3} Z_2^*} \right] \frac{1}{R^5} \\
& - \left[\frac{131\,220+53\,581.5\sqrt{6}}{Z_1^* Z_2^{*5}} + \frac{594\,864+243\,486\sqrt{6}}{Z_1^{*2} Z_2^{*4}} + \frac{927\,288+375\,921\sqrt{6}}{Z_1^{*3} Z_2^{*3}} \right. \\
& \quad \left. + \frac{594\,864+243\,486\sqrt{6}}{Z_1^{*4} Z_2^{*2}} + \frac{131\,220+53\,581.5\sqrt{6}}{Z_1^{*5} Z_2^*} \right] \frac{1}{R^7} + \dots, \quad (26)
\end{aligned}$$

$$\begin{aligned}
\Sigma_g^+(2P_1, 2P_{-1}) = & -\frac{9\sqrt{6}}{Z_1^* Z_2^* R^3} + \left[\frac{486-243\sqrt{6}}{Z_1^* Z_2^{*3}} + \frac{1620-486\sqrt{6}}{Z_1^{*2} Z_2^{*2}} + \frac{486-243\sqrt{6}}{Z_1^{*3} Z_2^*} \right] \frac{1}{R^5} \\
& + \left[\frac{-131\,220+53\,581.5\sqrt{6}}{Z_1^* Z_2^{*5}} + \frac{-594\,864+243\,486\sqrt{6}}{Z_1^{*2} Z_2^{*4}} + \frac{-927\,288+375\,921\sqrt{6}}{Z_1^{*3} Z_2^{*3}} \right. \\
& \quad \left. + \frac{-594\,864+243\,486\sqrt{6}}{Z_1^{*4} Z_2^{*2}} + \frac{-131\,220+53\,581.5\sqrt{6}}{Z_1^{*5} Z_2^*} \right] \frac{1}{R^7} + \dots, \quad (27)
\end{aligned}$$

In Figs. 6 and 7 we have plotted all nonzero energy curves between two hydrogen atoms in first excited states. Figure 6 also shows how the inclusion of exchange effects splits the singlet and triplet curves. The numerical values of the $^1\Delta_g$ and $^3\Delta_u$ state have been taken from the work of Linder and Hirschfelder.¹² The dashed curves are obtained from diagonal matrix elements, and the d placed behind the corresponding term symbol characterizes these energy curves. The effect of configuration

interaction is clear from a comparison of the two sets of curves. The $\Pi_u(2S, 2P_1)$ curve is not at all affected by configuration interaction, and the $\Pi_g(2S, 2P_1)_d$ differs only slightly from the exact one. On the other hand, the exact energy curve of the $\Pi_g(2P_1, 2P_0)$ state is repulsive; whereas the corresponding diagonal element shows an attractive potential.

Linder and Hirschfelder¹² have also calculated the electrostatic interaction energies between two hydrogen atoms in first excited states. Their Δ and Π state

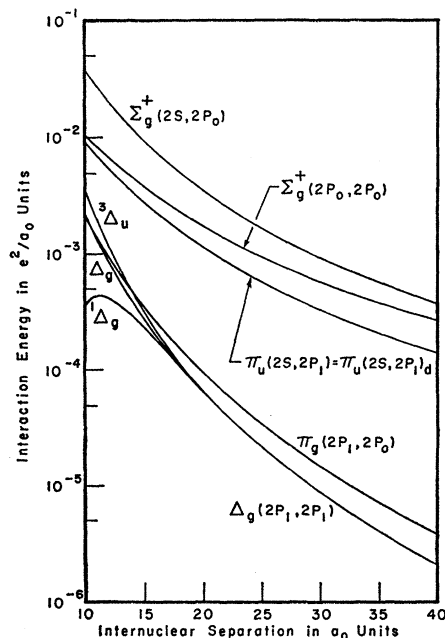


FIG. 6. Repulsive interaction energy curves between two hydrogen atoms in first excited states.

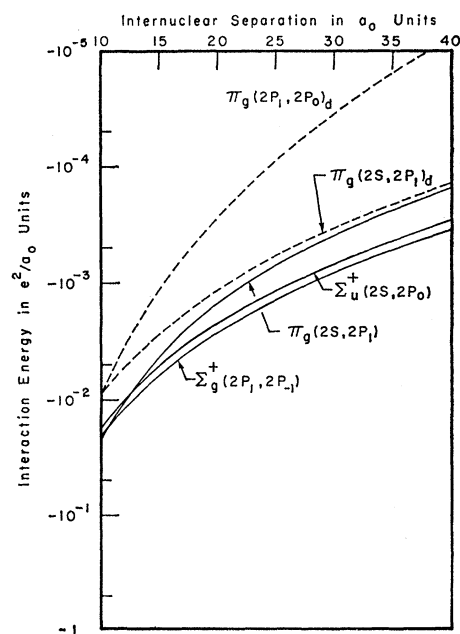


FIG. 7. Attractive interaction energy curves between two hydrogen atoms in first excited states. The dashed curves are obtained from diagonal matrix elements.

¹² B. Linder and J. O. Hirschfelder, J. Chem. Phys. 28, 197 (1958).

energies agree with (17)–(21) if we set $Z_1^* = Z_2^* = 1$. The last four Σ -state energies (24)–(27), however, differ from the ones in reference 12. The main discrepancy lies in the fact that the $\Sigma_g^+(2S, 2S)$ energy has an R^{-5} dependence in their series expansion and is zero in our case. This difference, moreover, affects all other energies which arise from the same secular determinant.

Some information about the origin of this discrepancy can be obtained by calculating the trace of that particular molecular sub-determinant and the one of the total secular determinant. From (24)–(27) we get $18/R^3 + 1296/R^5$ for the trace in the first case, and by adding up the energies of all the states of the degenerate set, we obtain zero for the secular determinant. In reference 12, on the other hand, the sum of the energies of the four Σ states gives $18/R^3 + 1395/R^5$ and the trace of the secular determinant is not zero.

All the matrix elements in the previous calculations contain only one multipole since the number of possible multipoles is determined from the C coefficient $C(la'; 000)$ which vanishes unless $a = l + l', \dots |l - l'|$ and the sum $l + a + l'$ is even. To illustrate the new feature of the competition of multipoles let us consider the states of a system consisting of one hydrogen atom in the first excited state and another one in the second excited state. From the interaction diagram in Fig. 1 which describes this case, we see that the Φ molecular subdeterminant is diagonal and made up of a Φ_g and Φ_u state.

The state functions for this case are obtained from (5). We can always write the interaction energy in the

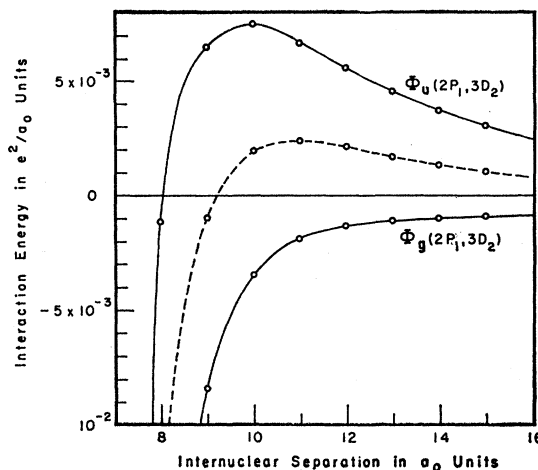


Fig. 8. The effect of the competition of multipoles on the energies of two Φ states formed by a hydrogen atom in the first excited state and a hydrogen atom in the second excited state. The dashed curve represents the nonresonance contribution.

form

$$E = E_{nr} \pm E_r, \quad (28)$$

where we have separated the contributions due to resonance (E_r) from those which can be obtained by using the simple product state functions (E_{nr}). In our example the plus sign in (28) yields the Φ_u state and the minus sign the Φ_g state. Here E_{nr} is made up of a quadrupole-quadrupole and a quadrupole- 2^4 pole term, and E_r consists of a dipole-dipole, dipole-octupole, octupole-dipole, and octupole-octupole term. Specifically:

$$\Phi_u(2P_1, 3D_2) = \frac{1.29600 \times 10^3}{Z_1^* Z_2^* R^5} - \frac{1.09350 \times 10^5}{Z_1^* Z_2^* R^7} + \frac{9.01737}{Z_1^* Z_2^* R^3} - \frac{3.11640 \times 10^2}{Z_1^* Z_2^* R^5} - \frac{3.11640 \times 10^2}{Z_1^* Z_2^* R^5} + \frac{2.69257 \times 10^4}{Z_1^* Z_2^* R^7}, \quad (29)$$

$\{^1\Phi_u, ^3\Phi_g\}$

and

$$\Phi_g(2P_1, 3D_2) = \frac{1.29600 \times 10^3}{Z_1^* Z_2^* R^5} - \frac{1.09350 \times 10^5}{Z_1^* Z_2^* R^7} - \frac{9.01737}{Z_1^* Z_2^* R^3} + \frac{3.11640 \times 10^2}{Z_1^* Z_2^* R^5} + \frac{3.11640 \times 10^2}{Z_1^* Z_2^* R^5} - \frac{2.69257 \times 10^4}{Z_1^* Z_2^* R^7}. \quad (30)$$

$\{^1\Phi_g, ^3\Phi_u\}$

In Fig. 8 we have plotted the interaction energies of these two states for $Z_1^* = Z_2^* = 1$ together with E_{nr} , the corresponding nonresonance contribution (dashed line). It is seen that due to the shorter range of the higher multipoles there is a pronounced competition between the multipoles at an internuclear separation of about $10a_0$. The Φ_u curve shows a distinct maximum which for the Φ_g state is much less pronounced and shifted to higher internuclear separations. Other states will be

attractive at large R and become repulsive at shorter separations. This could lead to bound states resulting entirely from electrostatic interactions. The inclusion of exchange forces will, of course, modify these energy curves to some extent, but since the maxima and minima occur at rather large internuclear separations, they very possibly may remain in a more complete calculation.

APPENDIX. EVALUATION OF THE RADIAL MATRIX ELEMENT

From (I-7) we see that the radial matrix element in (1) has the form

$$(n'l' | r^a | nl) = \left[\frac{(\gamma')^{3+2l'} (\gamma)^{3+2l}}{4n'n [\Gamma(n'+l'+1) \Gamma(n+l+1)]^3} \right]^{\frac{1}{2}} \times \int_0^\infty r^{l'+l+a+2} e^{-[(\gamma'+\gamma)/2]r} L_{n'-l'-1}^{2l'+1}(\gamma'r) L_{n-l-1}^{2l+1}(\gamma'r) dr, \quad (A-1)$$

where $\gamma' = 2me^2(Z')^*/\hbar^2 n'$. This integration can be carried out most easily using (I-8) which defines the Laguerre polynomials in terms of the Kummer confluent hypergeometric functions.

$$\begin{aligned} \langle n'l' | r^a | nl \rangle = & \left[\frac{(\gamma')^{3+2l'} (\gamma)^{3+2l}}{4n'n [\Gamma(n'+l'+1) \Gamma(n+l+1)]^3} \right]^{\frac{1}{2}} \\ & \times \Gamma(n'+l'+1) \Gamma(n+l+1) \Gamma(l'+l+a+3) (-)^{n'+n-l'-l} \binom{-2l'-2}{n'-l'-1} \binom{-2l-2}{n-l-1} \\ & \times \left(\frac{\gamma'+\gamma}{2} \right)^{-l'-l-a-3} F_2 \left(l'+l+a+3; -n'+l'+1, -n+l+1; 2l'+2, 2l+2; \frac{2\gamma'}{\gamma'+\gamma}, \frac{2\gamma}{\gamma'+\gamma} \right). \quad (\text{A-2}) \end{aligned}$$

F_2 , the generalized hypergeometric function of two variables is a special case of the Lauricella hypergeometric function F_A ¹³

$$F_A(\alpha; \beta_1 \cdots \beta_n; \gamma_1 \cdots \gamma_n; x_1 \cdots x_n) = \sum_{m_1 \cdots m_n} \frac{(\alpha, m_1+m_2+\cdots+m_n) (\beta_1, m_1) \cdots (\beta_n, m_n)}{(\gamma_1, m_1) \cdots (\gamma_n, m_n) (1, m_1) \cdots (1, m_n)} x_1^{m_1} \cdots x_n^{m_n}, \quad (\text{A-3})$$

with

$$(\lambda, k) = \Gamma(\lambda+k)/\Gamma(\lambda). \quad (\text{A-4})$$

The binomial coefficients in (A-2) can be written in the following way

$$\binom{-2l-2}{n-l-1} = \frac{\Gamma(-2l-1)}{\Gamma(n-l)\Gamma(-n-l)} = (-)^{n-l-1} \frac{\Gamma(n+l+1)}{\Gamma(2l+2)\Gamma(n-l)}. \quad (\text{A-5})$$

The last relation in (A-5) can be proved using the duplication formula for gamma functions. A similar equation holds for the binomial coefficient of the primed quantum numbers.

Substitution of (A-5) into (A-2) yields

$$\begin{aligned} \langle n'l' | r^a | nl \rangle = & \left[\frac{(\gamma')^{3+2l'} (\gamma)^{3+2l} \Gamma(n'+l'+1) \Gamma(n+l+1)}{4n'n \Gamma(n'-l') \Gamma(n-l)} \right]^{\frac{1}{2}} \left(\frac{\gamma'+\gamma}{2} \right)^{-l'-l-a-3} \frac{\Gamma(l'+l+a+3)}{\Gamma(2l'+2) \Gamma(2l+2)} \\ & \times F_2 \left(l'+l+a+3; -n'+l'+1, -n+l+1; 2l'+2, 2l+2; \frac{2\gamma'}{\gamma'+\gamma}, \frac{2\gamma}{\gamma'+\gamma} \right). \quad (\text{A-6}) \end{aligned}$$

Finally, by eliminating the γ 's and making use of (A-3), we get for the radial matrix element

$$\begin{aligned} \langle n'l' | r^a | nl \rangle = & 2^{3+l'+l} a_o^a \left[\frac{\left(\frac{Z^{*'}}{n'} \right)^{3+2l'} \left(\frac{Z^*}{n} \right)^{3+2l}}{4n'n} \Gamma(n'+l'+1) \Gamma(n+l+1) \Gamma(n'-l') \Gamma(n-l) \right]^{\frac{1}{2}} \left(\frac{Z^{*'}}{n'} + \frac{Z^*}{n} \right)^{-l'-l-a-3} \\ & \times \sum_{\xi, \eta=0}^{\infty} \frac{(-)^{\xi+\eta} \Gamma(l'+l+a+\xi+\eta+3)}{\Gamma(n'-l'-\xi) \Gamma(n-l-\eta) \Gamma(2l'+\xi+2) \Gamma(2l+\eta+2) \Gamma(\xi+1) \Gamma(\eta+1)} \\ & \times \left(\frac{2nZ^{*'}}{nZ^{*'}+n'Z^*} \right)^{\xi} \left(\frac{2n'Z^*}{nZ^{*'}+n'Z^*} \right)^{\eta}. \quad (\text{A-7}) \end{aligned}$$

In the calculation of first order interaction energies between nonidentical atoms, only those matrix elements are needed which satisfy the conditions: $n'=n$ and $Z^{*'}=Z^*$. In this case, the double sum in (A-7) degenerates into a single sum as can be shown by making use of the following equation¹⁴

$$F_2(\alpha; \beta, \beta'; \gamma, \gamma'; x, y) = \sum_{m=0}^{\infty} \frac{(\alpha, m) (\beta, m) (\beta', m)}{(\gamma, m) (\gamma', m) (1, m)} x^m y^m {}_2F_1(\alpha+m, \beta+m; \gamma+m; x) {}_2F_1(\alpha+m, \beta'+m; \gamma'+m; y), \quad (\text{A-8})$$

¹³ P. Appell, J. de Math. 3ème series, VIII, 173 (1882). P. Appell and M. J. Kampé de Fériet, *Fonctions Hypergéométriques et Hypersphériques; Polynômes d'Hermite* (Gauthier-Villars, Paris, 1926). J. Horn, Math. Ann. **105**, 381 (1931).

¹⁴ A. Erdélyi, W. Magnus, F. Oberhettinger, and G. F. Tricomi, *Higher Transcendental Functions*, Bateman Manuscript Project, (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 243.

where ${}_2F_1$ is the Gauss confluent hypergeometric function.¹⁵

$${}_2F_1(\alpha, \beta; \gamma; z) = \sum_{n=0}^{\infty} \frac{(\alpha, n)(\beta, n)}{(\gamma, n)(1, n)} z^n. \quad (\text{A-9})$$

From (A-6) we see that for $\gamma' = \gamma$, we have $x = y = 1$ and one can show that¹⁶

$${}_2F_1(\alpha, \beta; \gamma; 1) = \frac{\Gamma(\gamma)\Gamma(\gamma - \alpha - \beta)}{\Gamma(\gamma - \alpha)\Gamma(\gamma - \beta)}, \quad \Re(\gamma - \alpha - \beta) > 0. \quad (\text{A-10})$$

The result can be simplified by using the following relations between gamma functions:

$$\Gamma(-a+b)/\Gamma(-a) = (-)^b \Gamma(a+1)/\Gamma(a-b+1). \quad (\text{A-11})$$

Combining (A-10) with (A-8) and making use of (A-11), we get

$$\begin{aligned} (nl' | r^a | nl)_{Z^{*'}=Z^*} = & \frac{(-)^{l'+l} n^{a-1} a_o^a}{2^{a+1} Z^{*a}} \left[\frac{\Gamma(n-l')\Gamma(n-l)}{\Gamma(n+l'+1)\Gamma(n+l+1)} \right]^{\frac{1}{2}} \\ & \times \sum_{\xi=0}^{\infty} \frac{\Gamma(l'+l+a+3+\xi)\Gamma(l-l'+a+2)\Gamma(l'-l+a+2)}{\Gamma(n-l'-\xi)\Gamma(n-l-\xi)\Gamma(-n+l'+a+3+\xi)\Gamma(-n+l+a+3+\xi)\Gamma(\xi+1)}. \end{aligned} \quad (\text{A-12})$$

¹⁵ Reference 14, p. 248.

¹⁶ Reference 7, p. 6.