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Moderately Long-Range Interatomic Forces*

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The moderately long-range interaction energies of degenerate atoms for nonresonant cases have been studied throughout the moderately long-range region. Extensive tabulation of necessary parameters and atomic properties for the calculation of the first-order quadrupole–quadrupole interaction energies has been made. Higher multipole interactions also have been considered and it has been shown that the $1/R$ series of the first-order Coulombic interaction energies converges very fast throughout the long-range region for atoms in the ground configuration. The effects of atomic spin–orbit splitting have been considered explicitly. It has been shown that (Λ, S) coupling and intermediate coupling may be important for the interactions between B, C, O, Al, Si, and Sc atoms in the relatively short internuclear separation range. For other atoms, the (J_a, J_b) coupling scheme will give satisfactory results throughout the long-range region. The experimental determination of the moderately long-range interatomic forces from predissociation data also has been discussed.

The estimated van der Waals dispersion energies for the first-row atoms are shown to be of almost the same size as the quadrupole–quadrupole interaction energies at the separation of twice the sum of the atomic radii. It has been also shown that the leading term $[\mathcal{O}(\alpha^2/R^3)]$ of the magnetic interaction energy of two degenerate atoms is 10∼20% of the quadrupole–quadrupole interaction energy at $R=30a_0$ through the third-row atoms.

CONTENTS

I. INTRODUCTION

The calculation of interaction energies between atoms in ground and excited states has become of considerable interest. For the purpose of discussion, it is convenient to divide interatomic and intermolecular forces into short-, intermediate-, moderately long-, and long-range forces. The short-range forces are invariably repulsive and rise sharply with decreasing internuclear separation R. The forces in the intermediate range may be either attractive or repulsive; this is the region in which the exchange forces predominate. The moderately long-range forces take over at sufficiently large R where the charge distributions of the two interacting molecules do not overlap and yet not large enough to involve strong retardation effects, $R<\bar{\lambda}$. Here $\bar{\lambda}=(\alpha\Delta\epsilon)^{-1}$ is the reduced wavelength characteristic of allowed transitions in the interacting molecules ($\alpha=e^2/\hbar c\sim\frac{1}{137}$ is the fine structure constant and $\Delta\epsilon$ is the corresponding excitation energy). This region is usually associated with the dispersion forces arising from a second-order perturbation calculation. In some instances, as for example in the interaction of noble gas atoms, the moderately long-range forces are made up essentially of dispersion forces. However, when excited states are involved or neither one of two interacting atoms are in an S-state, the first-order perturbations, such as dipole–dipole and quadrupole–quadrupole interactions, may not vanish. These interactions may be the dominant forces. At sufficiently large R, the relativistic or magnetic intermolecular forces may play an important role. For $R\sim\bar{\lambda}$ or $R>\bar{\lambda}$, retardation effects are involved, and quantum electrodynamics often must be used to calculate accurate interaction energies.

All the macroscopic measurements involving second-virial coefficients, Joule–Thomson coefficients, viscosity, and index of refraction give only qualitative information around the van der Waals minimum, a region where the charge distributions already overlap appreciably, and where the exchange forces make a considerable contribution to the interaction energy. The recent advances in molecular beam techniques make it possible to determine the energy curves over a large range of internuclear separations. So far, however, precise experimental data are only available through the intermediate range. One reason for the scarcity of data at large internuclear separations is the need for an extremely small aperture and high resolution of detecting apparatus to test the long-range behavior of the energy curves. From the theoretical point of view, the intermediate range is very difficult to investigate, and the approximation methods needed to perform a reasonable calculation very often obscure the basic concepts. The interaction energies at large separations,

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on the other hand, can be calculated exactly by applying the perturbation theory.

Since potential energy curves play such an important role in the solution of many physical and chemical problems[1] it is essential to have available realistic potential energy functions. This is true particularly when dealing with degenerate ground states and excited states where the conventional semi-empirical formulas, such as the Lennard-Jones or Buckingham potentials, cannot be employed.

The present investigation is concerned with moderately long-range interactions between atoms with nonvanishing angular momenta. The first-order perturbation interaction between atoms in the ground configurations is investigated in detail. Special attention is paid to the investigation of the validity of various approximations, the validity and convergence of $1/R$-series expansions, the effect of atomic spin–orbit splitting, and the effects of higher multipole interactions. The second-order perturbation interactions and magnetic interactions of two atoms in degenerate states are also considered and will be compared with the first-order Coulombic interaction energy.

For the calculation of interatomic energy at large separation, it is convenient to consider three cases separately: the atomic spin–orbit splittings are (a) very large $[(J_a, J_b)$ coupling$]$, (b) negligible $[(\Lambda, S)$ coupling$]$, and (c) of the same order of magnitude (intermediate coupling) compared to the interaction energy. The quadrupole–quadrupole interaction energy, which is the leading term of the first-order Coulombic interaction for nonresonant cases, has been studied previously for atoms in the ground terms (case b) and in the ground levels[2] (case a) by Knipp[3] (1938). However, the intermediate case (case c) and other effects to the lead term described above had not been considered, and the atomic wave functions employed for the evaluation of necessary atomic properties were crude.

A complete set of potential energy curves arising from the interaction of two excited hydrogen atoms, with $2s$ and $2p$ electrons, has been given for intermediate to large separations by Linder and Hirschfelder.[4] They have obtained the accurate first-order perturbation energies, but the effects of atomic spin–orbit splittings at large separations have not been considered. Fontana[5] has studied interactions between hydrogen-like atoms (alkali atoms) in ground and excited states. He has considered cases (a), (b), and (c). Recently the relativistic or magnetic effects for the moderately long-range intermolecular forces has been studied systematically in the Breit–Pauli approximations by Meath and Hirschfelder.[6a] However, for the interactions of many-electron atoms in degenerate states, the potential energy curves at moderately long and long range have not been fully studied in detail.

Since we are concerned with degenerate systems, the application of degenerate perturbation theory to the calculation of moderately long-range interatomic forces (Coulombic and magnetic interactions) is described in Sec. II. The $1/R$-series expansion of the interaction energy of degenerate atoms is considered in detail.

Throughout the present work we assume that the Russell–Saunders coupling scheme holds in the states of the atoms of interest. For the evaluation of necessary atomic properties, we employ the Hartree–Fock atomic wave functions.

In Sec. III, the first-order electrostatic interaction of two atoms are considered. The symmetry-adapted molecular wave functions at large R are constructed for three different cases: (a) (J_a, J_b) coupling case (atomic spin–orbit splitting is very large compared to the interaction energy), (b) (Λ, S) coupling case (atomic spin–orbit splitting is small), and (c) (J_a, L_b) coupling case (atomic spin–orbit splitting is large in atom a and small in atom b). The construction of these wave functions has been considered previously by Knipp[3] for atoms in the ground term or ground levels. Here we will consider all possible cases. The evaluation of energy matrix elements is considered in detail for atomic orbital wave functions.

The secular equations are solved to obtain the first-order interaction energies and the correct zeroth-order wave functions for various cases. First, we consider the quadrupole–quadrupole interaction energy for three extreme cases $[(J_a, J_b)$, (Λ, S), and (J_a, L_b) coupling cases$]$. Next we consider the interactions of atoms with $(nd)^\mu$ and $(nf)^\mu$ configurations. It is noted that for this case higher multipole interaction terms in addition to the quadrupole–quadrupole term appear. The convergence of the $1/R$-series expansion of the first-order Coulombic interaction energies is studied.

Finally, we consider intermediate coupling cases where the atomic spin–orbit splitting becomes of the same order of magnitude as the interaction energies. To see which coupling scheme is applicable to the various ranges of R for different systems, we consider some potential energy curves of the systems B–B and C–O in detail as examples.

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[1] See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1964).

[2] Note that the energy levels of an atom may be thought of as arising from the various electron *configurations*. The electrostatic interactions split the configurations into *terms*, denoted by their L and S values, with different energies. The spin–orbit interaction splits each term into $2L+1$ or $2S+1$ energy *levels*, distinguished by their J values, which run from $|L+S|$ to $|L-S|$. Each of these energy levels is still degenerate, having $2J+1$ eigenfunctions corresponding to M values which run from J to $-J$.

[3] J. K. Knipp, Phys. Rev. **53**, 734 (1938).

[4] B. Linder and J. O. Hirschfelder, J. Chem. Phys. **28**, 197 (1958).

[5] (a) P. R. Fontana, Phys. Rev. **123**, 1871 (1961); (b) Phys. Rev. **125**, 1597 (1962).

[6] (a) W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. **44**, 3197 (1966); (b) W. J. Meath, J. Chem. Phys. **45**, 4519 (1966).

In Sec. IIID, we consider the experimental determination of the moderately long-range interatomic forces from the predissociation data. In particular, the predissociation data of the $b\ ^3\Sigma^+$ state of CO is analyzed in detail and compared with theoretical results.

In Sec. IV, the estimates of the van der Waals dispersion energies are made for the interactions of the first-row atoms and are compared with the quadrupole-quadrupole interaction energies of the corresponding systems. The magnetic interaction energies are also considered, and the range of R for which magnetic interaction energies become important is considered. In Sec. V, the new features of this work are summarized and the significance of the results is discussed.

Throughout the present work atomic units are used: energy$\sim e^2/a_0$, length$\sim a_0$, where e is electronic charge and a_0 is the Bohr radius.

II. GENERAL THEORY

The perturbations due to the (moderately) long-range intermolecular forces are truly small compared to the total energies of the isolated molecules so that the quantum-mechanical perturbation theory[7] is applicable and converges rapidly.

In this section we consider the Coulombic energy of interaction and the magnetic interaction energy between two atoms. The Coulombic energy of interaction may include all types of electrostatic, inductive, dispersive, and resonance force which do not involve the effects of electron exchange between the colliding atoms. By the magnetic interaction energy we mean the magnetic (or relativistic) interaction energy in the Breit–Pauli approximation.[6]

In our discussion, we neglect retardation effects[8] and thus we assume $R \ll \lambdabar$. Here $\lambdabar$ is the reduced wavelength characteristic of allowed transitions in the interacting atoms. The adiabatic coupling[9] between electronic and nuclear motion also will not be considered here.

A. Coulombic Interaction of Two Atoms

In the long-range interaction of two atoms,[10] a and b, the zeroth-order Hamiltonian H_0 will be

$$H_0 = H(a) + H(b), \qquad (2.1)$$

where $H(a)$ and $H(b)$ are the Hamiltonian operators for the isolated molecules a and b, respectively. The usual nonrelativistic Hamiltonian $H(a)$ for atom a with the nuclear charge Z_a can be written in the form

$$H(a) = -\tfrac{1}{2}\sum_{j=1}^{n_a} \nabla_j^2 - \sum_{j=1}^{n_a} \frac{Z_a}{r_{aj}} + \sum_{i>j} r_{ij}^{-1}, \qquad (2.2)$$

where n_a is the number of electrons, r_{aj} is the distance between nucleus a and electron j, and r_{ij} is the distance between electrons i and j. For the cases where the atomic spin–orbit splittings are larger than the interaction energies of two atoms, our atomic Hamiltonian may include the spin–orbit Hamiltonian[11] $H_{l\cdot s}(a)$:

$$H'(a) = H(a) + H_{l\cdot s}(a). \qquad (2.3)$$

The Hamiltonians $H(b)$ and $H'(b)$ for atom b are defined similarly.

The perturbation V acting between two atoms will be, in the present approximation, the sum of the Coulombic interactions between the electrons and nuclei associated with the different atoms. This can be written in the form

$$V = -\sum_{k=1}^{n_a} \frac{Z_b}{r_{bk}} - \sum_{j=1}^{n_b} \frac{Z_a}{r_{aj}} + \sum_{k=1}^{n_a} \sum_{j=1}^{n_b} r_{kj}^{-1} + \frac{Z_a Z_b}{R}, \qquad (2.4)$$

where R is the internuclear separation.

Let the functions $\phi_a(s_a t_a)$, $t_a = 1, 2, \cdots, g(s_a)$, belong to the $g(s_a)$-fold degenerate eigenvalue $\epsilon(s_a)$ of $H(a)$ and similarly for the eigenvalue $\epsilon(s_b)$ of $H(b)$. We have the functions $\phi_b(s_b t_b)$, $t_b = 1, 2, \cdots, g(s_b)$. Then our initial set for the $g(s_a)g(s_b)$-fold degenerate eigenvalue $\epsilon(s) = \epsilon(s_a) + \epsilon(s_b)$ of H_0 may be the functions

$$\chi_{st} = \phi_a(s_a t_a)\phi_b(s_b t_b), \qquad t_a = 1, 2, \cdots, g(s_a), \quad t_b = 1, 2, \cdots, g(s_b). \qquad (2.5)$$

For a complete treatment of interatomic forces it would be necessary to consider the more general wave functions which are antisymmetric with respect to the exchange of any two electrons. However, at large internuclear separation the exchange terms which result from interchanging electrons between the colliding atoms becomes negligibly small, and hence we will use the simple product functions (2.5) as the initial starting set. The proper zeroth-

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[7] For recent reviews of the perturbation theory, see (a) A. Dalgarno, in *Quantum Theory*, D. R. Bates, Ed. (Academic Press Inc., New York, 1961), Vol. 1, Chap. 5; (b) J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quantum Chem. **1**, 255 (1964).

[8] See, for example, (a) H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948); (b) C. Mavroyannis and M. J. Stephen, Mol. Phys. **5**, 629 (1962); (c) M. J. Stephen, J. Chem. Phys. **40**, 669 (1964); (d) R. R. McLone and E. A. Power, Proc. Roy. Soc. (London) **286**, 573 (1965); (e) M. R. Philpott, Proc. Phys. Soc. (London) **87**, 619 (1966).

[9] For nice discussions, see (a) T. Y. Wu and A. B. Bhatia, J. Chem. Phys. **24**, 48 (1956); T. Y. Wu, *ibid.* **24**, 444 (1956); (b) A. Dalgarno and R. McCarroll, Proc. Roy. Soc. (London) **A237**, 383 (1956); **A239**, 413 (1957); (c) D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. **32**, 1323 (1960); (d) A. Fröman, J. Chem. Phys. **36**, 1490 (1962); (e) W. R. Thorson, J. Chem. Phys. **37**, 433 (1962); (f) R. T. Pack, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-197, November 1966.

[10] The generalization to the interactions of two molecules or more than two molecules will be straightforward. See, for the discussion of the Coulombic interactions of two or three molecules, J. S. Dahler and J. O. Hirschfelder, J. Chem. Phys. **25**, 986 (1956).

[11] For nice discussions and detailed calculations of spin–orbit coupling in atoms, see (a) M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962); (b) Proc. Roy. Soc. (London) **A271**, 565 (1963); (c) M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. **134**, A320 (1964).

order wave functions $\psi_{st}^{(0)}$, $t=1, 2, \cdots, g(s)\equiv g(s_a)g(s_b)$, can be obtained by solving the secular equation. The perturbed energy can be written in the form

$$E_{st}=\epsilon(s)+E_{st}^{(1)}+E_{st}^{(2)}+\cdots, \tag{2.6}$$

where

$$\begin{aligned} E_{st}^{(1)} &= \langle\psi_{st}^{(0)} \mid V \mid \psi_{st}^{(0)}\rangle \\ &= \sum_{t_a,t_b}\sum_{t_a',t_b'} \langle\phi_a(s_at_a)\phi_b(s_bt_b)\mid V \mid \phi_a(s_at_a')\phi_b(s_bt_b')\rangle\langle\phi_a(s_at_a')\phi_b(s_bt_b')\mid \psi_{st}^{(0)}\rangle\langle\psi_{st}^{(0)} \mid \phi_a(s_at_c)\phi_b(s_bt_b)\rangle \end{aligned} \tag{2.7}$$

is the first-order electrostatic and resonance energies. $E_{st}^{(2)}$ is usually written as a sum of the dispersion and induction energies,

$$E_{st}^{(2)}=E_{st}^{(2)}(\text{dis})+E_{st}^{(2)}(\text{ind}), \tag{2.8}$$

where

$$E_{st}^{(2)}(\text{dis})=\sum_{u_a\neq s_a,u_b\neq s_b}\frac{\sum_{v_a,v_b}\left|\sum_{t_a,t_b}\langle\psi_{st}^{(0)}\mid\phi_a(s_at_a)\phi_b(s_bt_b)\rangle\langle\phi_a(s_at_a)\phi_b(s_bt_b)\mid V\mid\phi_a(u_av_a)\phi_b(u_bv_b)\rangle\right|^2}{[\epsilon(s_a)-\epsilon(u_a)]+[\epsilon(s_b)-\epsilon(u_b)]} \tag{2.9}$$

and

$$\begin{aligned} E_{st}^{(2)}(\text{ind}) = &\sum_{u_a\neq s_a}\frac{\sum_{v_a,v_b}\left|\sum_{t_a,t_b}\langle\psi_{st}^{(0)}\mid\phi_a(s_at_a)\phi_b(s_bt_b)\rangle\langle\phi_a(s_at_a)\phi_b(s_bt_b)\mid V\mid\phi_a(u_av_a)\phi_b(s_bv_b)\rangle\right|^2}{[\epsilon(s_a)-\epsilon(u_a)]} \\ &+\sum_{u_b\neq s_b}\frac{\sum_{v_a,v_b}\left|\sum_{t_a,t_b}\langle\psi_{st}^{(0)}\mid\phi_a(s_at_a)\phi_b(s_bt_b)\rangle\langle\phi_a(s_at_a)\phi_b(s_bt_b)\mid V\mid\phi_a(s_av_a)\phi_b(u_bv_b)\rangle\right|^2}{[\epsilon(s_b)-\epsilon(u_b)]}. \end{aligned} \tag{2.10}$$

The interaction energy $E_{st}(ab)$ is given by

$$E_{st}(ab)=E_{st}-[\epsilon(s_a)+\epsilon(s_b)]. \tag{2.11}$$

It is well known that an expansion of the interaction energy in a series of inverse powers of the interatomic separation R is very convenient for long-range cases. The advantage of the R^{-1} expansion is that most of the individual energy terms involve the properties of the isolated atoms such as polarizability, net charge, dipole moment, quadrupole moment, etc. However, some of the interaction terms do require a knowledge of less familiar atomic properties.

Let us assume that $R>(R_a+R_b)$. Here R_a is the "radius" of atom a, such that most of the charge distribution of atom a lies within a sphere of radius R_a about its center. Similarly R_b is the "radius" of molecule b. Then the interaction potential V [Eq. (2.4)] can be expanded[12] in powers of R^{-1}:

$$V=\sum_{m=1}^{\infty}\frac{V_m}{R^m}. \tag{2.12}$$

The expansion coefficients V_m represent the interaction of the various electrostatic multipoles of atom a with those of molecule b. For example, V_1 represents the charge–charge interaction, V_2 the charge–dipole interaction, V_3 the dipole–dipole and charge–quadrupole interactions, etc. For the interaction of neutral atoms V_1 and V_2 are zero and the expansion for V simplifies considerably, with the result

$$V=\sum_{m=3}^{\infty}\frac{V_m}{R^m}, \tag{2.13}$$

$$V_m=\sum_{k=1}^{n_a}\sum_{j=1}^{n_b}\sum_{l_1=1}^{m-2}\sum_{m_1=-l_<}^{l_<}G(l_1, m_1)Y_{l_1}^{m_1}(\theta_k, \phi_k)Y_{m-l_1-1}^{-m_1}(\theta_j, \phi_j), \tag{2.14}$$

where $l_<$ is the lesser of l_1 and $m-l_1-1$, and the coefficient G is given by

$$G(l_1, m_1)=\frac{4\pi(-1)^{l_2}(l_1+l_2)!r_k^{l_1}r_j^{l_2}}{[(2l_1+1)(2l_2+1)(l_1-m_1)!(l_1+m_1)!(l_2-m_1)!(l_2+m_1)!]^{1/2}}. \tag{2.15}$$

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[12] (a) M. E. Rose, J. Math. Phys. **37,** 215 (1958); (b) B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **46,** 626 (1950); (c) R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83,** 628 (1951); **85,** 149 (1952).

Considering Eq. (2.13), the nth-order wave function and the nth-order energy may be written in the forms

$$\psi_{st}^{(n)}=\sum_{m=3n}^{\infty}\frac{\psi_{st}^{(n,m)}}{R^m},\tag{2.16}$$

and

$$E_{st}^{(n)}=\sum_{m=3n}^{\infty}\frac{E_{st}^{(n,m)}}{R^m}.\tag{2.17}$$

It will be shown first that the first-order energy $E_{st}^{(1)}$ and the zeroth-order wave functions $\psi_{st}^{(0)}$ may be an infinite series in R^{-1} for the interactions of atoms in degenerate states. The matrix elements v_{ml} in Eq. (A1) can be written in the form by use of Eq. (2.13)

$$v_{ml}=\sum_{s}\frac{v_{ml}(s)}{R^s}.\tag{2.18}$$

It can be seen, from the discussion in the Appendix, that if more than one term of v_{ml} in Eq. (2.18) do not vanish, $E_{st}^{(1)}$ and $\psi_{st}^{(0)}$ are infinite series in R^{-1}. From the symmetry consideration, it can be shown that the first-order energy $E_{st}^{(1)}$ will be an odd power series in R^{-1} and the zeroth-order wave function $\psi_{st}^{(0)}$ will be an even power series in R^{-1} (see Sec. IIIC2). Thus $E_{st}^{(1)}$ and $\psi_{st}^{(0)}$ in general can be written in the forms

$$E_{st}^{(1)}=\frac{E_{st}^{(1,3)}}{R^3}+\frac{E_{st}^{(1,5)}}{R^5}+\frac{E_{st}^{(1,7)}}{R^7}+\cdots,\tag{2.19}$$

and

$$\psi_{st}^{(0)}=\psi_{st}^{(0,0)}+\frac{\psi_{st}^{(0,2)}}{R^2}+\frac{\psi_{st}^{(0,4)}}{R^4}+\cdots.\tag{2.20}$$

Now to consider the first-order wave function and the second-order energy we introduce Eqs. (2.13), (2.19), and (2.20) into the first-order perturbation equation, and we obtain

$$[H_0-\epsilon(s)]\psi_{st}^{(1)}+\left[\left(\frac{V_3}{R^3}+\frac{V_4}{R^4}+\cdots\right)-\left(\frac{E_{st}^{(1,3)}}{R^3}+\frac{E_{st}^{(1,5)}}{R^5}+\cdots\right)\right]\left(\psi_{st}^{(0,0)}+\frac{\psi_{st}^{(0,2)}}{R^2}+\cdots\right)=0.\tag{2.21}$$

From Eq. (2.21), it is obvious that $\psi_{st}^{(1)}$ can be written as

$$\psi_{st}^{(1)}=\frac{\psi_{st}^{(1,3)}}{R^3}+\frac{\psi_{st}^{(1,4)}}{R^4}+\frac{\psi_{st}^{(1,5)}}{R^5}+\cdots.\tag{2.16a}$$

Substituting Eq. (2.16a) into Eq. (2.21) we obtain the following perturbation equations for various orders in R^{-1}:

$$(H_0-\epsilon(s))\psi_{st}^{(1,3)}+(V_3-E_{st}^{(1,3)})\psi_{st}^{(0,0)}=0,\tag{2.22}$$

$$(H_0-\epsilon(s))\psi_{st}^{(1,4)}+V_4\psi_{st}^{(0,0)}=0,\tag{2.23}$$

$$(H_0-\epsilon(s))\psi_{st}^{(1,5)}+(V_5-E_{st}^{(1,5)})\psi_{st}^{(0,0)}+(V_3-E_{st}^{(1,3)})\psi_{st}^{(0,2)}=0,\tag{2.24}$$

and so on. The second-order energy is given by

$$E_{st}^{(2)}=\frac{E_{st}^{(2,6)}}{R^6}+\frac{E_{st}^{(2,8)}}{R^8}+\frac{E_{st}^{(2,10)}}{R^{10}}+\cdots,\tag{2.25}$$

where

$$\begin{aligned}
E_{st}^{(2,6)}&=\langle\psi_{st}^{(0,0)}\mid V_3\mid\psi_{st}^{(1,3)}\rangle,\\
E_{st}^{(2,8)}&=\langle\psi_{st}^{(0,0)}\mid V_4\mid\psi_{st}^{(1,4)}\rangle+\langle\psi_{st}^{(0,2)}\mid V_3\mid\psi_{st}^{(1,3)}\rangle,\\
E_{st}^{(2,10)}&=\langle\psi_{st}^{(0,0)}\mid V_5\mid\psi_{st}^{(1,5)}\rangle+\langle\psi_{st}^{(0,2)}\mid V_4\mid\psi_{st}^{(1,4)}\rangle+\langle\psi_{st}^{(0,4)}\mid V_3\mid\psi_{st}^{(1,3)}\rangle.
\end{aligned}\tag{2.26}$$

The terms in odd powers of R^{-1} in $E_{st}^{(2)}$ vanish from the symmetry. Similarly the higher-order energies and wave functions can be investigated.

If we now assume, for the interaction energy $E_{st}(ab)$ and the total wavefunction Ψ_{st}, the following forms,

$$E_{st}(ab)=\sum_{m=3}^{\infty}C_m/R^m\tag{2.27}$$

and

$$\Psi_{st}=\sum_{m=0}^{\infty}\psi_{st}(m)/R^m.\tag{2.28}$$

The coefficients C_m and $\psi_{st}(m)$ are given by

$$C_m=\sum_{n=1}^{I}E_{st}^{(n,m)},\tag{2.29}$$

$$\psi_{st}^{(m)}=\sum_{n=0}^{I}\psi_{st}^{(n,m)},\tag{2.30}$$

where I is an integer such that $3I\leq n\leq 3(I+1)$. It is interesting to note that for the interaction of two neutral atoms, we have

$$\begin{aligned}
&C_3=E_{st}^{(1,3)};\quad C_4=0;\quad C_5=E_{st}^{(1,5)};\\
&C_6=E_{st}^{(2,6)};\quad C_7=E_{st}^{(1,7)};\quad C_8=E_{st}^{(2,8)};\\
&C_9=E_{st}^{(1,9)}+E_{st}^{(3,9)};\quad C_{10}=E_{st}^{(2,10)}.
\end{aligned}\tag{2.31}$$

For the nonresonant interactions, C_3 and $E_{st}^{(3,9)}$ are identically zero.

So far we have not considered the convergence of series (2.27). This series, in fact, diverges for all R and many attempts have been made to remove the divergence. Brooks[13] has pointed out that the divergence arises from the integration over portions of configuration space in which the expansion of the electrostatic energy is not valid. Dalgarno and Lewis[14] have, however, shown that the divergence is not due to the use of an expansion of the perturbation potential in regions of space where it is not valid, and it is a fundamental property of such series.

In spite of these remarks the expansion of the interatomic energy in a power series of R^{-1} is a very convenient one, and the first few leading terms give very good approximations to the correct one for many cases. It will be shown, however, that for the interactions of atoms in degenerate states the expansions such as Eq. (2.27) cannot be obtained at some region of interatomic separation (see Sec. IIIC3)—for example, the case where the atomic spin-orbit splittings and the quadrupole–quadrupole interaction energy are of the same order of magnitude.

B. Magnetic Interaction of Two Atoms

The systematic study of relativistic or magnetic intermolecular forces in the Breit–Pauli approximation has been recently made by Meath and Hirschfelder.[6] In the present brief discussions, particular attention will be paid to the interactions of two atoms in the degenerate states.

We start from the generalized Breit–Pauli Hamiltonian[1,6]:

$$H=H_e+\alpha^2 H_{\mathrm{rel}}, \tag{2.32}$$

where α is the fine structure constant, $\alpha=e^2/\hbar c\sim\frac{1}{137}$, and the nonrelativistic Hamiltonian H_e is given by

$$H_e=H(a)+H(b)+V. \tag{2.33}$$

$H(a)$, $H(b)$, and V are defined by Eqs. (2.2) and (2.4). The relativistic correction H_{rel} includes terms which allow for magnetic interactions between the electrons in the system and has the form[1]

$$H_{\mathrm{rel}}=H_{LL}+H_{SS}+H_{SL}+H_p+H_D. \tag{2.34}$$

Explicit expressions for the various terms in (2.34) are given elsewhere[1,6] and they have the following significance: H_{LL} corresponds to the interaction of the orbital magnetic moments of the electrons in the system; H_{SS} gives the interaction between the spin magnetic moments of the electrons; H_{SL} represents the interaction between the spin magnetic moments and the orbital magnetic moments of the electrons in the system; H_p is a relativistic correction due to the variation of electron mass with velocity; and H_D appears to have no simple interpretation.

If Ψ and E_e are the electronic nonrelativistic wave function and energy

$$H_e\Psi=E_e\Psi, \tag{2.35}$$

then the relativistic correction to E_e, correct through $O(\alpha^2)$, is

$$\mathcal{E}^{(1)}=\alpha^2\langle\Psi\mid H_{\mathrm{rel}}\mid\Psi\rangle. \tag{2.36}$$

For most practical purposes, this accuracy is sufficient.[15]

If the charge distributions of the interacting atoms a and b do not overlap, then the relativistic Hamiltonian H_σ, $\sigma=LL$, SS, SL, P, and D, can also be expanded[6a,16] in powers of R^{-1}:

$$H_\sigma=\sum_{m=0}^{\infty}H_{\sigma,m}/R^m;\qquad H_{\sigma,0}=H_{\sigma,0}(a)+H_{\sigma,0}(b). \tag{2.37}$$

Here $H_{\sigma,0}(a)$ and $H_{\sigma,0}(b)$ are the Hamiltonians for the isolated atoms a and b, and

$$H_{SL,1}=H_{SS,1}=H_{SS,2}=0;\qquad H_{p,m}=H_{D,m}=0,\qquad m>0. \tag{2.38}$$

The expansion coefficients $H_{\sigma,m}$, for $m>0$, represent the interaction of various orbital and spin magnetic multipoles of atom a with those of atom b.

When the perturbation α^2H_{rel} is much smaller than the perturbation V, then the nonrelativistic problem $H_e\Psi=E_e\Psi$ is first solved by use of Rayleigh–Schrödinger perturbation theory, as discussed in Sec. IIA. If we now use the multipole expansion for the relativistic Hamiltonian [Eq. (2.37)] and Eq. (2.28), the relativistic correction energy can be expanded in powers of R^{-1}:

$$\mathcal{E}_{\sigma,st}^{(1)}=\langle\Psi_{st}\mid H_\sigma\mid\Psi_{st}\rangle=\sum_{i=0}^{\infty}\frac{D_{\sigma,i}}{R^i},$$
$$\sigma=LL,\ SS,\ SL,\ P,\text{ and }D, \tag{2.39}$$

where

$$D_{\sigma,i}=\sum_{j=0}^{i}\sum_{k=0}^{i-j}\langle\psi_{st}(k)\mid H_{\sigma,j}\mid\psi_{st}(i-j-k)\rangle. \tag{2.40}$$

It should be noted[6a] that certain terms in $D_{\sigma,i}$ are identically zero, namely, $D_{SL,1}=D_{SS,1}=D_{SS,2}=D_{P,i>0}=D_{D,i>0}=0$, and $D_{LL,1}$, $D_{LL,2}$, $D_{SL,2}$, and $D_{SS,2}$ are not zero in general and may become the lead terms in the R^{-1} expansion of the interaction energy of two neutral atoms. However, it has been shown by Meath[6b] that, for nonresonant interaction of atoms, $D_{LL,1}$ and $D_{\sigma,2}$ are also zero and the interaction energy through $\mathcal{O}(\alpha^2/R^3)$ is identically equal to the semiclassical result.

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[13] F. C. Brooks, Phys. Rev. **86**, 92 (1952).

[14] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **A69**, 57 (1956).

[15] For example, see G. G. Hall and A. T. Amos, "Molecular Orbital Theory of the Spin Properties of Conjugated Molecules" in *Advances in Atomic and Molecular Physics*, D. R. Bates and I. Estermann, Eds. (Academic Press Inc., New York, 1965), Vol. 1, p. 2.

[16] P. R. Fontana and W. J. Meath, J. Math. Phys. (to be published).

Hence the lead term of magnetic interaction is $O(\alpha^2/R^3)$ for degenerate neutral atoms, while the lead term is $O(\alpha^2/R^4)$ for nondegenerate neutral atoms.

As R becomes larger, the perturbations V and $\alpha^2 H_{\mathrm{rel}}$ may become the same order of magnitude. In this case, we have to apply both perturbations V and $\alpha^2 H_{\mathrm{rel}}$ simultaneously to the appropriate zeroth-order problem. As already pointed out, the R^{-1} expansion of the interaction energy may not be possible for this range of R.

At the sufficiently large R the relativistic interaction energy can be much larger than the nonrelativistic Coulombic interaction energy since there are nonvanishing terms of lower orders of $1/R$ in the relativistic interaction energy. In this case, the perturbation scheme will be reversed: first apply the perturbation $\alpha^2 H_{\mathrm{rel}}$ to the appropriate zeroth-order problem, and from the resulting wave functions the Coulombic interaction energy may be obtained.

III. FIRST-ORDER COULOMBIC INTERACTION OF TWO ATOMS

In this section, the first-order Coulombic interaction energy between two atoms in degenerate states is investigated in detail. We consider only nonresonant cases. First, the construction of molecular wave functions at large internuclear separation is considered in detail. Then secular equations are solved to obtain the first-order energy for various cases. The atomic spin-orbit coupling effect, the effect of higher multipole interaction, and the validity of the R^{-1}-expansion of interaction energies are considered in detail for actual systems. Extensive tabulation of necessary parameters and atomic properties for calculating the first-order electrostatic interaction energies are also made.

A. Coulombic Interaction Operator

When two atoms are far enough apart that overlapping and consequent exchange effects are negligible, the interaction can be considered as being composed of mixed terms of different pole strength, as discussed already. Since we consider nonresonant cases the first nonvanishing first-order energies are the quadrupole–quadrupole interaction energies. Nonvanishing first-order dipole–dipole interaction energy is obtained only if the atoms are like and are in states with different parity (resonance forces[17]). If the atoms have $(np)^\mu$ configuration, the only nonvanishing first-order terms will be the quadrupole–quadrupole interaction energies. For atoms with $(nd)^\mu$ configurations, the quadrupole–2^4-pole and 2^4-pole–2^4-pole interaction energies also do not vanish. It should be noted that if either atom has spherical symmetry (S state), the first-order interaction energy is identically zero in nonresonant cases.

The Coulombic interaction potential V for the interaction of two neutral atoms has been given in a power series of R^{-1} at large separation [Eq. (2.13)]. We consider only nonvanishing first-order interaction terms in nonresonant cases explicitly here. This can be written in the form

$$V'=\frac{W_5}{R^5}+\frac{W_7}{R^7}+\frac{W_9+W_9'}{R^9}+\cdots, \tag{3.1}$$

where

$$W_5=\sum_{m=-2}^{2} a_5(m)Q_2^m(a)Q_2^{-m}(b), \tag{3.2}$$

$$W_7=\sum_{m=-2}^{2} a_7(m)(1+P_{ab})Q_2^m(a)Q_4^{-m}(b), \tag{3.3}$$

$$W_9=\sum_{m=-4}^{4} a_9(m)Q_4^m(a)Q_4^{-m}(b), \tag{3.4a}$$

$$W_9'=\sum_{m=-2}^{2} a_9'(m)(1+P_{ab})Q_2^m(a)Q_6^{-m}(b), \tag{3.4b}$$

$Q_l^m(p)$, $a_{l+k+1}(m)$, and P_{ab} being defined by

$$Q_l^m(p)=[4\pi/(2l+1)]^{1/2}\sum_k r_{pk}{}^l Y_l^m(\theta_{pk},\phi_{pk})$$
$$=\sum_k q_l^m(k), \tag{3.5}$$

$$a_{l+k+1}(\pm m)$$
$$=(l+k)!/[(l-m)!(l+m)!(k-m)!(k+m)!]^{1/2}, \tag{3.6}$$

$$P_{ab}h(a,b)=h(b,a). \tag{3.7}$$

The functions $Q_l^m(p)$, $m=-l, -l+1, \cdots, l$, have the property that they form the 2l+1 dimensional irreducible representation of the three-dimensional rotation group, and hence are an irreducible spherical tensor operator of rank l. This property is very helpful in evaluating matrix elements.

B. Zeroth-Order Wave Functions and Energy Matrix Elements

We construct here the symmetry-adapted initial starting functions χ_j which factorize the secular determinant significantly. The symmetries of the system of two interacting atoms are those of rotations around the internuclear line, reflections in planes through this line, and, in the case of like nuclei of inversion, that is reflections in the midpoint between the nuclei, holding the nuclei fixed. The possible molecular states and their relation to the states of the atoms when widely separated have been considered in detail by Wigner and Witmer.[18]

1. *Spin-Orbit Splitting Large*

We assume that the Russell-Saunders coupling scheme holds in the states of the atoms of interest.

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[17] For example, see Ref. 1, p. 990 *et seq.*

[18] (a) E. Wigner and E. E. Witmer, Z. Physik. **51**, 859 (1928); also see (b) F. Hund, Z. Physik. **63**, 723 (1930); (c) R. S. Mulliken, Phys. Rev. **36**, 1440 (1930); (d) Rev. Mod. Phys. **4**, 1 (1932); (e) Ref. 3; (f) G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950).

When the spin–orbit splitting of the atomic term energies is large compared to the interaction energies, the *SLJM* scheme is most suitable for the atomic states.[19] The molecule (two interacting atoms) has a quantum number Ω for the absolute value of the total angular momentum along the internuclear axis. This case may be called (J_a, J_b) coupling [this is called (J_1, J_2) coupling in Herzberg[18f]], and will be considered in more detail since the resulting functions are more widely used in our work.

Since we are neglecting the electron exchange we can use, as the zeroth-order wave functions for the interacting atoms, simple products[20] of the atomic wave functions. We define the functions

$$\varphi(J_aJ_bM_aM_b)=\phi_a(J_aM_a)\phi_b(J_bM_b), \tag{3.8}$$

where ϕ_a and ϕ_b are the normalized wave functions for atoms a and b, representing the states in specific energy levels. Let

$$d=\omega_a\omega_b(-)^{J_a+J_b}, \tag{3.9}$$

where ω_a and ω_b are the parities of atoms a and b, respectively.

Unlike atoms. In case of two unlike atoms the functions for $\Omega\neq0$

$$\chi(J_aJ_b\Omega M_a)=\varphi(J_aJ_bM_a, \Omega-M_a),\ d(-)^{\Omega}\chi(J_aJ_b, -\Omega, -M_a) \tag{3.10}$$

are partners belonging to the two rows of the representation of the two-dimensional rotation–reflection group. For a given Ω, M_a takes on the values $(J_a\geq J_b)$:

$$\begin{aligned} &J_a+J_b\geq\Omega\geq J_a-J_b+1 \qquad M_a=J_a, J_a-1, \cdots, \Omega-J_b \\ &J_a-J_b\geq\Omega>0 \qquad M_a=\Omega+J_b, \Omega+J_b-1, \cdots, \Omega-J_b. \end{aligned} \tag{3.11}$$

For $\Omega=0$ we introduce the two sets of functions

$$\chi(J_aJ_b(\pm)M_a)=\sqrt{2}^{-1}[\varphi(J_aJ_bM_a, -M_a)\pm d\varphi(J_aJ_b, -M_a, M_a)] \qquad M_a=J_b, J_b-1, \cdots, >0,\ (J_a>J_b), \tag{3.12}$$

where $\chi(+)$ represents 0^+ state and $\chi(-)$ represents 0^- state. If J_a and J_b are integers, we have in addition

$$\chi(J_aJ_b(\beta)0)=\varphi(J_aJ_b00), \tag{3.13}$$

$\chi(\beta)$ being positive (0^+) if $d=1$ and negative (0^-) if $d=-1$.

The matrix V' [cf. Eq. (3.1)] is diagonal in Ω, and plus and minus for $\Omega=0$. Let

$$\langle\varphi(J_aJ_bM_aM_b)\mid W_s\mid\varphi(J_a'J_b'M_a'M_b')\rangle\equiv\langle J_aJ_bM_aM_b\mid W_s\mid J_a'J_b'M_a'M_b'\rangle,$$

where W_s are defined by Eqs. (3.2)–(3.5), and so on. The matrices $\mathbf{W}_s$ can be expressed in the forms

$$\langle\chi(J_aJ_b\Omega M_a)\mid W_s\mid\chi'(J_a'J_b'\Omega M_a')\rangle=\langle J_aJ_bM_a, \Omega-M_a\mid W_s\mid J_a'J_b'M_a', \Omega-M_a'\rangle, \tag{3.14a}$$

$$\begin{aligned}\langle\chi(J_aJ_b(\pm)M_a)\mid W_s\mid\chi'(J_a'J_b'(\pm)M_a')\rangle=&\langle J_aJ_bM_a, -M_a\mid W_s\mid J_a'J_b'M_a', -M_a'\rangle\\ &\pm d\langle J_aJ_b, -M_a, M_b\mid W_s\mid J_a'J_b'M_a', -M_a'\rangle,\end{aligned} \tag{3.14b}$$

$$\langle\chi(J_aJ_b(\beta)0)\mid W_s\mid\chi'(J_a'J_b'(\beta)M_a')\rangle=\sqrt{2}\langle J_a'J_b'M_a', -M_a'\mid W_s\mid J_aJ_b00\rangle, \tag{3.14c}$$

$$\langle\chi(J_aJ_b(\beta)0)\mid W_s\mid\chi'(J_a'J_b'(\beta)0)\rangle=\langle J_aJ_b00\mid W_s\mid J_a'J_b'00\rangle. \tag{3.14d}$$

Like atoms. We consider first the case of like atoms in the same levels (atoms in states of the same configuration and term and the same J values). Let

$$f=(-)^n\omega_a\omega_b, \tag{3.15}$$

where n is the number of electrons of an atom. For like atoms in the same levels $(J_a=J_b\equiv J)$, we define the functions[18a,20]

$$\begin{aligned}&\chi(JJ_u^g\Omega M_a)=\sqrt{2}^{-1}[\varphi(JJM_a, \Omega-M_a)\pm f\varphi(JJ, \Omega-M_a, M_a)],\\ &M_a=J, J-1, \cdots, >\tfrac{1}{2}\Omega.\end{aligned} \tag{3.16}$$

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[19] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1963), Chaps. 7 and 8.

[20] It is, however, noted that actual molecular wave functions should be antisymmetrical in all the electrons. Therefore, we will assume that, for the consideration of symmetry properties of molecular wave functions, the function $\phi(a, b)$ defined by Eqs. (3.8), (3.35), (3.36), and (3.51) are antisymmetrical: That is,

$$\phi(a, b)=\mathcal{A}\phi_a\phi_b,$$

where ϕ_a and ϕ_b are the normalized atomic wave functions and

$$\mathcal{A}=[n_a!n_b!/(n_a+n_b)!]^{1/2}[1+(-)^pP_{ab}].$$

Here P_{ab} interchanges electrons between atoms a and b, and p is the parity of P_{ab}. Also, see the discussion in Ref. 3.

If J is an integer and Ω is even, or if J is a half-integer and Ω is odd, we have in addition

$$\chi(JJ\delta\Omega\tfrac{1}{2}\Omega)=\varphi(JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega). \tag{3.17}$$

$\chi(g)$ represents gerade state and $\chi(u)$ ungerade state. $\chi(\delta)$ is gerade if $f=1$ and ungerade if $f=-1$. For $\Omega=0$ the g states are positive and u states are negative.

Next we consider like atoms which are not in the same levels. We define the functions for $\Omega\neq 0$

$$\chi(J_aJ_b{}^{g}_{u}\Omega M_a)=\sqrt{2}^{-1}[\varphi(J_aJ_bM_a,\Omega-M_a)\pm f\varphi(J_bJ_a,\Omega-M_a,M_a)]. \tag{3.18}$$

For a given value of Ω, possible values of M_a are given by Eq. (3.11). When $\Omega=0$, we define the functions

$$\chi(J_aJ_b(\pm)^{g}_{u}M_a)=\tfrac{1}{2}[(\varphi(J_aJ_bM_a,-M_a)\pm f\varphi(J_bJ_a,-M_a,M_a))\pm d(\varphi(J_aJ_b,-M_a,M_a)\pm f\varphi(J_bJ_aM_a,-M_a))],$$
$$M_a=J_b,\qquad J_b-1,\cdots>0. \tag{3.19}$$

If J_a and J_b are integers we have in addition for $\Omega=0$

$$\chi(J_aJ_b(\beta)^{g}_{u}0)=\sqrt{2}^{-1}[\varphi(J_aJ_b00)\pm f\varphi(J_bJ_a00)] \tag{3.20}$$

where β is positive if $d=1$ and negative if $d=-1$.

The matrices $\mathbf{W}_s$ are diagonal in Ω, g, and u, and plus and minus for $\Omega=0$. The elements of matrices $\mathbf{W}_s$ can be written in the forms

$$\langle\chi(J_aJ_b{}^{g}_{u}\Omega M_a)|W_s|\chi'(J_a'J_b'{}^{g}_{u}\Omega M_a')\rangle=\langle J_aJ_bM_a,\Omega-M_a|W_s|J_a'J_b'M_a',\Omega-M_a'\rangle$$
$$\pm f\langle J_aJ_bM_a,\Omega-M_a|W_s|J_b'J_a',\Omega-M_a',M_a'\rangle, \tag{3.21a}$$

$$\langle\chi(J_aJ_b(\pm)^{g}_{u}M_a)|W_s|\chi'(J_a'J_b'(\pm)^{g}_{u}M_a')\rangle=\langle J_aJ_bM_a,-M_a|W_s|J_a'J_b'M_a',-M_a'\rangle$$
$$\pm f\langle J_aJ_bM_a,-M_a|W_s|J_b'J_a',-M_a',M_a'\rangle\pm d[\langle J_aJ_bM_a,-M_a|W_s|J_a'J_b',-M_a',M_a'\rangle$$
$$\pm f\langle J_aJ_bM_a,-M_a|W_s|J_b'J_a'M_a',-M_a'\rangle], \tag{3.21b}$$

$$\langle\chi(JJ^{g}_{u}0M_a)|W_s|\chi'(J_a'J_b'{}^{(+)g}_{(-)u}M_a')\rangle$$
$$=\sqrt{2}(\langle JJM_a,-M_a|W_s|J_a'J_b'M_a',-M_a'\rangle\pm f\langle JJM_a,-M_a|W_s|J_b'J_a',-M_a',M_a'\rangle), \tag{3.21c}$$

$$\langle\chi(JJ^{g}_{u}0M_a)|W_s|\chi'(J_a'J_b'(\beta)^{g}_{u}0)\rangle=2\langle JJM_a,-M_a|W_s|J_a'J_b'00\rangle, \tag{3.21d}$$

$$\langle\chi(JJ\delta\Omega\tfrac{1}{2}\Omega)|W_s|\chi'(J_a'J_b'{}^{g}_{u}\Omega M_a')\rangle=\sqrt{2}\langle JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega|W_s|J_a'J_b'M_a',\Omega-M_a'\rangle, \tag{3.21e}$$

$$\langle\chi(JJ\delta00)|W_s|\chi'(J_a'J_b'{}^{(+)g}_{(-)u}M_a')\rangle=2\langle JJ00|W_s|J_a'J_b'M_a',-M_a'\rangle, \tag{3.21f}$$

$$\langle\chi(JJ\delta00)|W_s|\chi'(J_a'J_b'(\beta)^{g}_{u}0)\rangle=\sqrt{2}\langle JJ00|W_s|J_a'J_b'00\rangle, \tag{3.21g}$$

$$\langle\chi(J_aJ_b(\beta)^{g}_{u}0)|W_s|\chi'(J_a'J_b'(\pm)^{g}_{u}M_a')\rangle=\sqrt{2}(\langle J_aJ_b00|W_s|J_a'J_b',M_a',-M_a'\rangle\pm\langle J_aJ_b00|W_s|J_b'J_a',-M_a',M_a'\rangle). \tag{3.21h}$$

Evaluation of $\langle J_aJ_bM_aM_b|W_s|J_a'J_b'M_a'M_b'\rangle$. Using the expressions of W_s given in Sec. IIIA and applying the Wigner–Eckart theorem[21] we obtain

$$\langle J_aJ_bM_aM_b|W_s|J_a'J_b'M_a'M_b'\rangle=\sum_m a_s(m)\{1+h(K,L)P_{ab}\}\{\langle J_aM_a|Q_K{}^m(a)|J_a'M_a'\rangle\langle J_bM_b|Q_L{}^{-m}(b)|J_b'M_b'\rangle\}$$
$$=\sum_m a_s(m)\{1+h(K,L)P_{ab}\}\{C(J_a'KJ_a;M_a'mM_a)\langle J_a\|Q_K\|J_a'\rangle$$
$$\times C(J_b'LJ_b;M_b',-m,M_b)\langle J_b\|Q_L\|J_b'\rangle\}, \tag{3.22}$$

where $h(K,L)$ is defined as

$$h(K,L)=0\qquad\text{if } K=L,$$
$$h(K,L)=1\qquad\text{if } K\neq L, \tag{3.23}$$

$C(J_1J_2J_3;\,m_1m_2m_3)$ are the Clebsch–Gordan coefficients,[22] and $\langle J_1\|Q_L\|J_1'\rangle$ are the reduced matrix elements[21] of the set of tensor operators $Q_L{}^m$. The Clebsch–Gordan coefficient $C(J_1J_2J_3;\,m_1m_2m_3)$ vanishes unless J_1, J_2, and J_3

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[21] For example, see M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 85.

[22] For example, see Ref. 21, p. 32 *et seq.* Also see Ref. 19, p. 73 *et seq.*

satisfy a triangular condition and $m_3=m_1+m_2$. Hence we have the relations from Eq. (3.22)

$$m=M_a-M_a'; \qquad -m=M_b-M_b', \tag{3.24}$$

and hence

$$M_a+M_b=M_a'+M_b'. \tag{3.25}$$

Therefore, all matrix elements vanish unless $M_a+M_b=M_a'+M_b'$, and thus the total angular momentum $\mathbf{J}=\mathbf{J}_a+\mathbf{J}_b$ is quantized along the internuclear axis with components M_a+M_b. The secular determinent is factored into subdeterminants which can be classified by the molecular quantum number Ω, as already pointed out. Eq. (3.22) can now be written in the form

$$\begin{aligned}\langle J_aJ_bM_aM_b \mid W_s \mid J_a'J_b'M_a'M_b'\rangle=&\delta(M_a+M_b, M_a'+M_b')a_s(M_a-M_a')\{1+h(K, L)P_{ab}\}\\ &\times\{C(J_a'KJ_a; M_a', M_a-M_a', M_a)C(J_b'LJ_b; M_b', M_b-M_b', M_b)\langle J_a \| Q_K \| J_a'\rangle\langle J_b \| Q_L \| J_b'\rangle\},\end{aligned} \tag{3.26}$$

where $\delta(M, M')$ is the Kronecker delta.

Now to evaluate the reduced matrix element we start from the Wigner–Eckart theorem

$$\langle JM \mid Q_K^0 \mid J'M\rangle=C(J'KJ; M0M)\langle J \| Q_K \| J'\rangle. \tag{3.27}$$

To obtain the explicit expression, we transform to the zeroth-order representation scheme[19] characterized by one-electron quantum numbers $u\equiv nlm_lm_s$. If U stands for the collection of such quantum numbers in a zeroth-order state of the atom, we have

$$C(J'KJ; M0M)\langle J \| Q_K \| J'\rangle=\sum_{U,U'}\langle\gamma SLJM \mid U\rangle\langle U \mid Q_K^0 \mid U'\rangle\langle U' \mid \gamma'S'L'J'M\rangle, \tag{3.28}$$

where γ designates quantum numbers other than S, L, J, and M. Since Q_L^M is a sum of one-electron operators q_l^m [cf. Eq. (3.5)], $\langle U \mid Q_K^0 \mid U'\rangle$ vanishes if U' differs from U by more than one individual electron quantum number set. If all sets but $u\neq u'$ are the same, $\langle U \mid Q_K^0 \mid U'\rangle=\langle u \mid q_K^0 \mid u'\rangle$, and for $U=U'$, $\langle U \mid Q_K^0 \mid U\rangle=\sum_u\langle u \mid q_K^0 \mid u\rangle$. Hence Eq. (3.28) becomes

$$\begin{aligned}C(J'KJ; M0M)\langle J \| Q_K \| J'\rangle=&\sum_U\{\langle\gamma SLJM \mid U\rangle\langle U \mid \gamma'S'L'J'M\rangle\sum_u\langle u \mid q_K^0 \mid u\rangle\}\\ &+\sum_{U,U'}\{\langle\gamma SLJM \mid U\rangle\langle U' \mid \gamma'S'L'J'M\rangle\langle u \mid q_K^0 \mid u'\rangle\},\end{aligned} \tag{3.29}$$

where U' has the same sets of individual electron quantum numbers but $u\neq u'$. The matrix elements $\langle u \mid q_L^0 \mid u'\rangle$ can be easily evaluated by using the properties of spherical harmonics[23]:

$$\begin{aligned}\langle u \mid q_L^0 \mid u'\rangle&=\langle nlm_lm_s \mid q_L^0 \mid n'l'm_l'm_s\rangle\\ &=[(2l'+1)/(2l+1)]C(l'Ll; 000)C(l'Ll; m_l'0m_l)\langle nl \mid r^L \mid n'l'\rangle,\end{aligned} \tag{3.30}$$

where

$$\langle nl \mid r^L \mid n'l'\rangle=\int_0^\infty dr\, r^{L+2}R(nl)R'(n'l'),$$

$R(nl)$ being the radial part of the wave function for an electron in an nl state. Furthermore, it can be shown that

$$\sum_{m=-l}^{l} C(lLl; m0m)=0, \qquad L>0. \tag{3.31}$$

To show this we use the following properties for the C coefficients[24]:

$$C(j_1j_2j_3; m_1m_2m_3)=(-)^{j_1-m_1}[(2j_3+1)/(2j_2+1)]^{1/2}C(j_1j_3j_2; m_1, -m_3, -m_2), \tag{3.32a}$$

$$C(jj0; m, -m, 0)=(-)^{j-m}(2j+1)^{-1/2}, \tag{3.32b}$$

$$\sum_{m_1} C(j_1j_2j; m_1, m-m_1, m)C(j_1j_2j'; m_1, m-m_1, m)=\delta_{jj'}. \tag{3.32c}$$

By use of Eq. (3.32a), the sum at the left-hand side in Eq. (3.31) can be written as

$$\sum_{m=-l}^{l}(-)^{l-m}[(2l+1)/(2L+1)]^{1/2}C(llL; m, -m, 0),$$

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[23] For example, see Ref. 21, p. 62.

[24] See Ref. 21, Chap. III.

and using Eqs. (3.32b) and (3.32c) we find

$$\frac{2l+1}{(2L+1)^{1/2}}\sum_{m=-l}^{l} C(llL;\,m,\,-m,\,0)C(ll0;\,m,\,-m,\,0)=\delta_{L0}. \tag{3.31a}$$

This proves Eq. (3.31). Therefore, for the sum $\sum_u\langle u\mid q_L{}^0\mid u\rangle$ in Eq. (3.29), the part summed over the electrons in complete shells gives zero, and contributions to the sum will come only from incomplete shells. The explicit expression for $\langle J\,||\,Q_K\,||\,J'\rangle$ can be obtained from Eqs. (3.29) and (3.30).

When the unprimed and primed states in $\langle J\,||\,Q_K\,||\,J'\rangle$ represent atomic states in the levels which come from the same term, the second sum in Eq. (3.29) vanishes, since if all but one of the m_l are the same, they must all be the same because of the condition $\sum m_l=\sum m_l'=M$ for U and U'. Hence, for this case, the reduced matrix elements can be written as the following form, assuming that there exists only one incomplete shell (nl):

$$\langle J\,||\,Q_K\,||\,J'\rangle=D_K(JJ')\langle r^K\rangle_{nl}, \tag{3.33}$$

where

$$D_K(JJ')=\frac{C(lKl;\,000)}{C(J'KJ;\,M0M)}\sum_U\{\langle\gamma SLJM\mid U\rangle\langle U\mid\gamma SLJ'M\rangle\sum_{m_l}C(lKl;\,m_l0m_l)\}, \tag{3.34}$$

the sum over m_l being made for the incomplete shell (nl), and $\langle r^K\rangle_{nl}=\langle nl\mid r^K\mid nl\rangle$. From Eq. (3.31) and symmetry property

$$C(j_1j_2j_3;\,m_1m_2m_3)=(-)^{j_1+j_2-j_3}C(j_1j_2j_3;\,-m_1,\,-m_2,\,-m_3),$$

it can be shown that $D_K(JJ')$ for the shells, which is complete except for ν missing electrons, have the opposite sign of those for shells which have ν electrons.

2. *Spin-Orbit Splitting Negligible*

When the atomic spin-orbit splitting is negligible compared to the interaction energy, the SLM_SM_L scheme is applicable to the atomic states.[19] The system of two interacting atoms will have quantum numbers Λ and Σ for the absolute value of the total orbital angular momentum and the total spin along the axis and S for the total spin. This is called $(\Lambda,\,S)$ coupling. Let $\mathbf{S}$ be the total spin of the system, with the corresponding quantum number S. Then possible values of S are S_a+S_b, S_a+S_b-1, $\cdots$, $|\,S_a-S_b\,|$. We define the functions[20]

$$\varphi_{ab}(S\Sigma M_L{}^aM_L{}^b)=\sum_{M_s{}^a}\phi_a(S_aL_aM_S{}^aM_L{}^a)\phi_b(S_bL_b,\,\Sigma-M_S{}^a,\,M_L{}^b)C(S_aS_bS;\,M_S{}^a,\,\Sigma-M_S{}^a,\,\Sigma), \tag{3.35}$$

$$\varphi_{ba}(S\Sigma M_L{}^aM_L{}^b)=\sum_{M_s{}^a}\phi_a(S_bL_b,\,\Sigma-M_S{}^a,\,M_L{}^b)\phi_b(S_aL_aM_S{}^aM_L{}^a)C(S_bS_aS;\,\Sigma-M_S{}^a,\,M_S{}^a\Sigma), \tag{3.36}$$

and

$$c=\omega_a\omega_b(-)^{L_a+L_b}. \tag{3.37}$$

Here ϕ_a and ϕ_b are the normalized wave functions for atoms a and b, representing the states in the corresponding terms. The coefficients C in Eqs. (3.35) and (3.36) are the Clebsch-Gordan coefficients.

Unlike atoms. For two interacting unlike atoms, the functions for $\Lambda\neq0$

$$\chi(S\Sigma\Lambda M_L)=\varphi_{ab}(S\Sigma M_L,\,\Lambda-M_L),\;c(-)^\Lambda\chi(S\Sigma,\,-\Lambda,\,-M_L) \tag{3.38}$$

are partners belonging to the two rows of the Λth representation of the two-dimensional rotation-reflection group. For given Λ, M_L takes on the following values $(L_a\geq L_b)$:

$$\begin{aligned}&L_a+L_b\geq\Lambda\geq L_a-L_b+1 \qquad M_L=L_a,\,L_a-1,\,\cdots,\,\Lambda-L_b;\\&L_a-L_b\geq\Lambda>0, \qquad M_L=\Lambda+L_b,\,\Lambda+L_b-1,\,\cdots,\,\Lambda-L_b.\end{aligned} \tag{3.39}$$

For $\Lambda=0$ we have

$$\begin{aligned}\chi(S\Sigma(\pm)M_L)&=\sqrt{2}^{-1}[\varphi_{ab}(S\Sigma M_L,\,-M_L)\pm c\varphi_{ab}(S\Sigma,\,-M_L,\,M_L)] \qquad M_L=L_b,\,L_b-1,\,\cdots>0\\ \chi(S\Sigma(\beta)0)&=\varphi_{ab}(S\Sigma00).\end{aligned} \tag{3.40}$$

The functions $\chi(+)$ represent Σ^+ states and $\chi(-)$ represents Σ^- states. $\chi(\beta)$ represents Σ^+ if $c=1$ and Σ^- if $c=-1$.

The matrices $\mathbf{V}'$ are diagonal in S, Σ, and Λ (also positive and negative for $\Lambda=0$). The diagonality in S and Σ results from the fact that V' is independent of the spin coordinates.

Like atoms. The case of like atoms in the states of the same configuration and term will be considered first. Let

$$e=(-)^S. \tag{3.41}$$

We define the functions[18a,20]

$$\chi(S\Sigma_u^g\Lambda M_L)=\sqrt{2}^{-1}[\varphi_{ob}(S\Sigma M_L,\ \Lambda-M_L)\pm e\varphi_{ab}(S\Sigma,\ \Lambda-M_L,\ M_L)] \qquad M_L=L_a,\ L_a-1,\ \cdots,\ \tfrac{1}{2}\Lambda, \tag{3.42}$$

and in addition, if Λ is even,

$$\chi(S\Sigma\delta\Lambda\tfrac{1}{2}\Lambda)=\varphi_{ab}(S\Sigma\tfrac{1}{2}\Lambda\tfrac{1}{2}\Lambda). \tag{3.43}$$

Here $\chi(g)$ is gerade and $\chi(u)$ is ungerade. $\chi(\delta)$ is g if $e=1$ and u if $e=-1$. For $\Lambda=0$, negative states are g if S is odd $(e=-1)$, and u if S is even $(e=1)$, while positive states are g if S is even and u if S is odd.

Next we consider like atoms which are not in the same terms. We define the functions for $\Lambda\neq0$

$$\chi(S\Sigma_u^g\Lambda M_L)=\sqrt{2}^{-1}[\varphi_{ab}(S\Sigma M_L,\ \Lambda-M_L)\pm f\varphi_{ba}(S\Sigma M_L,\ \Lambda-M_L)], \qquad f=(-)^n(-)^{S_a+S_b-S}\omega_a\omega_b, \tag{3.44}$$

where, for a given value of Λ, possible values of M_L are given by Eq. (3.39), and n is the number of electron in an atom. For $\Lambda=0$, we define the functions

$$\chi(S\Sigma(\pm)_u^gM_L)=\tfrac{1}{2}[(\varphi_{ab}(S\Sigma M_L,\ -M_L)\pm f\varphi_{ba}(S\Sigma M_L,\ -M_L))\pm c(\varphi_{ab}(S\Sigma,\ -M_L,\ M_L)\pm f\varphi_{ba}(S\Sigma,\ -M_L,\ M_L))]$$

$$M_L=L_b,\ L_b-1,\ \cdots>0 \qquad (L_a\geq L_b), \tag{3.45}$$

$$\chi(S\Sigma(\beta)_u^g0)=\sqrt{2}^{-1}[\varphi_{ab}(S\Sigma00)\pm f\varphi_{ba}(S\Sigma00)]. \tag{3.46}$$

Here β is positive (Σ^+) if $c=1$ and negative (Σ^-) if $c=-1$.

The matrices $\mathbf{W}_s$ are diagonal in S, Σ, Λ (also positive and negative for $\Lambda=0$), and g and u. The matrices $\mathbf{W}_s$ can be expressed in terms of the integral

$$\langle\varphi(S\Sigma M_L{}^aM_L{}^b)\mid W_s\mid\varphi'(S\Sigma M_L{}^{a'}M_L{}^{b'})\rangle\equiv\langle S\Sigma M_L{}^aM_L{}^b\mid W_s\mid S\Sigma M_L{}^{a'}M_L{}^{b'}\rangle. \tag{3.47}$$

Because of the unitary characters of the Clebsch–Gordan coefficients in Eq. (3.35) and the fact that W_s is independent of the spin, the integral (3.47) can be written in the form

$$\begin{aligned}
&\langle S\Sigma M_L{}^aM_L{}^b\mid W_s\mid S\Sigma M_L{}^{a'}M_L{}^{b'}\rangle\\
&\quad=\sum_m a_s(m)\{1+h(K,L)P_{ab}\}\{\langle L_aM_L{}^a\mid Q_K{}^m\mid L_a'M_L{}^{a'}\rangle\langle L_bM_b\mid Q_L{}^{-m}\mid L_b'M_L{}^{b'}\rangle\}\\
&\quad=\delta(M_L{}^a+M_L{}^a,\ M_L{}^{a'}+M_L{}^{b'})a_s(M_L{}^a-M_L{}^{a'})\{1+h(K,L)P_{ab}\}\\
&\qquad\times\{C(L_a'KL_a;\ M_L{}^{a'},\ M_L{}^a-M_L{}^{a'},\ M_L{}^a)C(L_b'LL_b;\ M_L{}^{b'},\ M_L{}^b-M_L{}^{b'},\ M_L{}^b)\\
&\qquad\times\langle L_a\parallel Q_K\parallel L_a'\rangle\langle L_b\parallel Q_L\parallel L_b'\rangle\}.
\end{aligned} \tag{3.48}$$

The last step has been obtained by using the Wigner–Eckart theorem[21] and the properties of the Clebsch–Gordan coefficients[22] as for $\langle J_aJ_bM_aM_b\mid W_s\mid J_a'J_b'M_a'M_b'\rangle$ in Sec. IIIB1. The reduced matrix elements $\langle L\parallel Q_K\parallel L'\rangle$ can be evaluated by the similar method, as used for $\langle J\parallel Q_K\parallel J'\rangle$. When we are considering only the states which are from the same term and we assume that there exists only one incomplete shell (nl), $\langle L\parallel Q_K\parallel L\rangle$ are found to be:

$$\langle L\parallel Q_K\parallel L\rangle=C_K(LL)\langle r^K\rangle_{nl}, \tag{3.49}$$

where

$$C_K(LL)=\frac{C(lKl;\,000)}{C(LKL;\,M_L0M_L)}\sum_U\{|\langle\gamma SLM_sM_L\mid U\rangle|^2\sum_{m_l}C(lKl;\,m_l0m_l)\}, \tag{3.50}$$

the sum over m_l being made for the incomplete shell (nl). $D_2(JJ)$ [Eq. (3.34)] and $C_2(LL)$ [Eq. (3.50)] for the quadrupole–quadrupole interactions has already been derived by Knipp.[3]

3. *Spin–Orbit Splitting Large in One Atom and Negligible in the Other*

Knipp[3] has also considered, for the quadrupole–quadrupole interaction, the case of two different atoms in one of which the atomic spin-orbit splitting is large and in the other it is negligible. This case may be called (J_a, L_b) coupling. Introducing the new functions[20]

$$\varphi(J_aS_bM_S{}^bM_aM_L{}^b)=\phi_a(J_aM_a)\phi_b(M_S{}^bM_L{}^b), \tag{3.51}$$

we can define the functions

$$\chi(J_aS_bM_S{}^b\Gamma M_a)=\varphi(J_aS_bM_S{}^bM_a,\ \Gamma-M_a) \tag{3.52}$$

for $\Gamma\neq 0$. Here Γ is a new quantum number for the present system. If J_a is an integer, Γ can in addition take zero, for which value we define the functions

$$\chi(J_aS_bM_S{}^b{}_\beta{}^\alpha M_a)=\sqrt{2}^{-1}[\varphi(J_aS_bM_S{}^bM_a,\,-M_a)\mp\varphi(J_aS_bM_S{}^b,\,-M_a,\,M_a)],\qquad M_a\neq 0;$$

$$\chi(J_aS_bM_S{}^b\beta 0)=\varphi(J_aS_bM_S{}^b00). \tag{3.53}$$

The matrices $\mathbf{W}_k$ are diagonal in $M_S{}^b$ and Γ (also α and β for $\Gamma=0$). The matrix elements

$$\langle\varphi(J_aS_bM_S{}^bM_aM_L{}^b)\,|\,W_k\,|\,\varphi'(J_a'S_bM_S{}^bM_a'M_L{}^{b\prime})\rangle\equiv\langle J_aM_aM_L{}^b\,|\,W_k\,|\,J_a'M_a'M_L{}^{b\prime}\rangle \tag{3.54}$$

is found to be

$$\begin{aligned}\langle J_aM_aM_L{}^b\,|\,W_k\,|\,J_a'M_a'M_L{}^{b\prime}\rangle&\\ &=\sum_m a_k(m)\{1+h(K,L)P_{ab}\}\{\langle J_aM_a\,|\,Q_K{}^m\,|\,J_a'M_a'\rangle\langle L_bM_L{}^b\,|\,Q_L{}^{-m}\,|\,L_b'M_L{}^{b\prime}\rangle\}\\ &=\delta(M_a+M_L{}^b,\,M_a'+M_L{}^{b\prime})a_k(M_a-M_a')\{1+h(K,L)P_{ab}\}\\ &\qquad\times\{C(J_a'KJ_a;\,M_a',\,M_a-M_a',\,M_a)C(L_b'LL_b;\,M_L{}^{b\prime},\,M_L{}^b-M_L{}^{b\prime},\,M_L{}^b)\\ &\qquad\qquad\times\langle J_a\,\|\,Q_K\,\|\,J_a'\rangle\langle L_b\,\|\,Q_L\,\|\,L_b'\rangle\}.\end{aligned} \tag{3.55}$$

The reduced matrix elements appearing in Eq. (3.55) have been already considered.

C. Solution of Secular Equation

In this subsection, the first-order interatomic energies are calculated. Our calculations will be restricted to the cases of atoms with only one incomplete shells, in particular, atoms in the ground terms, since for these cases quite general formulae can be obtained and accurate atomic wave functions are applicable for most atoms of interest.

1. Quadrupole–Quadrupole Interaction for Extreme Cases

For nonresonant cases, the first nonvanishing first-order electrostatic interaction energies are the quadrupole–quadrupole interaction energies, and hence these terms are the most important. By extreme cases we mean: (a) atomic spin-orbit splittings are very large in both atoms [hence strict $(J_a,\,J_b)$ coupling is applicable], (b) it is negligible in both atoms [hence strict $(\Lambda,\,S)$ coupling is applicable], and (c) it is negligible in one atom and very large in the other [hence $(J_a,\,L_b)$ coupling is applicable] compared to the interaction energy. For these cases, the starting zeroth-order wave functions χ_j have been already constructed in Sec. IIIB, and the evaluation of the energy matrix elements also has been discussed. For $(J_a,\,J_b)$ coupling case, we may need to consider only χ_j arising from atomic states in specific levels (see Sec. IIIB1) for $(\Lambda,\,S)$ coupling case χ_j arising from atomic states in specific terms (see Sec. IIIB2) and for $(J_a,\,L_b)$ coupling case χ_j arising from atomic states, one of which is in a specific level and the other in a specific term (see Sec. IIIB3).

For the quadrupole–quadrupole interaction of two unlike atoms in any state and like atoms in the same terms or the same levels, the elements of the matrix $\mathbf{W}_5$ [Eq. (3.2)] have as a common factor the product of two reduced matrix elements. Dividing by this factor, we obtain a dimensionless secular determinant. In general let K_a, K_b be a pair of integer or half-integers corresponding to J_a, J_b; L_a, L_b; or J_a, L_b. Let ζ stand for Ω, Λ, or Γ. The range of the remaining parameter (M_L or M) is essentially the same in all three cases. It can be shown that the dimensionless determinant obtained by dividing out the products of reduced matrix elements is the same for all three cases. Furthermore, for unlike atoms with $K_a=K_b$, we can form linear combinations $\chi(g)$ and $\chi(u)$ which are formally the same as for like atoms. It can be shown that $\mathbf{W}_5$ has no cross terms between these two groups and hence the dimensionless determinant is the same as for like atoms. Therefore, we have the simple result that the dimensionless determinant depends only on the numerical values of the pair of numbers K_a, K_b. We designate the roots of secular determinant by $\alpha(K_aK_b\zeta)$. Hence for three extreme cases of two unlike atoms in any states and like atoms in the same terms or the same levels, the quadrupole–quadrupole interaction energy is given by one of the expressions

$$\alpha(J_aJ_b\Omega)D_2(J_aJ_a)D_2(J_bJ_b)\langle r_a{}^2\rangle\langle r_b{}^2\rangle/R^5, \tag{3.56a}$$

$$\alpha(L_aL_b\Lambda)C_2(L_aL_a)C_2(L_bL_b)\langle r_a{}^2\rangle\langle r_b{}^2\rangle/R^5, \tag{3.56b}$$

$$\alpha(J_aL_b\Gamma)D_2(J_aJ_a)C_2(L_bL_b)\langle r_a{}^2\rangle\langle r_b{}^2\rangle/R^5. \tag{3.56c}$$

Here $D_2(JJ)$ and $C_2(LL)$ have been defined by Eqs. (3.34) and (3.50), and $\langle r_a{}^2\rangle$ and $\langle r_b{}^2\rangle$ are the mean-square radii of the incomplete shells of atoms a and b, respectively. $\alpha(K_aK_b\zeta)$ for some values of K_a and K_b, $C_2(LL)$ for ground terms of atoms, and $D_2(JJ)$ for ground levels have been calculated by Knipp.[3] We give more extensive tables here. $\alpha(K_aK_b\zeta)$ are given in

TABLE I. $\alpha(K_aK_b\tau)$ for integral K and integral τ. In (J_a, J_b) coupling, e means gerade and f means ungerade for like atoms in the same level; a means that the state is positive if $d\equiv\omega_a\omega_b(-)^{J_a+J_b}=1$, negative if $d=-1$, while b means that the state is positive if $d=-1$, negative if $d=1$. In (Λ, S) coupling, a means that the state is positive if $c\equiv\omega_a\omega_b(-)^{L_a+L_b}=1$, negative if $c=-1$, while b means that the state is positive if $c=-1$, negative if $c=1$; for like atoms in the same term, e means gerade (g) if the molecular spin (S) is even, ungerade (u) if S is odd, while f means g if S is odd, u if S is even.

	$K_a=1$	2	2	3	3
τ	$K_b=1$	1	2	1	2
0	3.6*ea* 0.0*ea*	2.3235*a* −0.2951*a*	3.2609*ea* 1.5085*ea* −0.4836*ea*	2.0963*a* −0.3816*a*	2.2881*a* 1.3105*a* −0.9074*a*
	0.0*fb*	−1.0142*b*	2.7738*fb* −1.0595*fb*	−1.2247*b*	1.4169*b* −1.2099*b*
1	−2.4*e*	2.4529 0.0477 −1.4864	1.1269*e* −1.4126*e*	2.0609 −0.1696 −1.4014	3.1386 1.2765 0.9434 −1.0193 −1.4409
	0.0*f*		1.2033*f* −0.9166*f*		
2	0.6*e*	0.3558 −2.8912	0.8571*e* −1.8571*e*	2.1980 0.2300 −1.9381	1.0557 0.1412 −1.4873 −1.7798
			−2.0*f*		
3		1.0142	−2.5714*e*	0.6461 −3.0956	0.9888 −1.9539 −2.3472
			0.8571*f*		
4			1.7143*e*	1.2247	1.2502 −2.2853
5					2.0702

	$K_a=3$	4	4	4	4
τ	$K_b=3$	1	2	3	4
0	3.5471*ea* 1.7713*ea* 1.2456*ea* −1.1641*ea*	2.0135*a* −0.4180*a*	2.0084*a* 1.2489*a* −1.1733*a*	2.5104*a* 1.4801*a* 1.0216*a* −1.3406*a*	3.8728*ea* 2.1160*ea* 1.4486*ea* 0.5766*ea* −1.4452*ea*
	3.4602*fb* 0.7780*fb* −1.2382*fb*	−1.3054*b*	0.9575*b* −1.3253*b*	2.1778*b* 0.4612*b* −1.3363*b*	3.8606*fb* 1.5166*fb* 0.2742*fb* −1.4202*fb*
1	1.8874*e* 0.5249*e* −1.3457*e*	1.9716 −0.2890 −1.3925	2.2842 1.2657 0.7933 −1.1216 −1.5055	3.6374 1.6848 1.3841 0.8276 0.2848 −1.3351 −1.5095	2.3036*e* 1.3172*e* 0.1852*e* −1.4839*e*
	1.4859*f* 1.1490*f* −1.3016*f*				2.1276*f* 1.4266*f* 0.4349*f* −1.5112*f*
2	1.2080*e* 0.2294*e* −1.7040*e*	1.9241 0.0297 −1.6636	3.1472 1.1697 0.3958 −1.2783 −1.7182	1.3485 1.2746 0.3274 −0.1083 −1.5079 −1.7883	1.3869*e* 1.0815*e* −0.0030*e* −1.7018*e*
	−0.1667*f* −1.6667*f*				0.6819*f* −0.0729*f* −1.6726*f*

TABLE I. (*Continued*)

τ	$K_a=3$	4	4	4	4
	$K_b=3$	1	2	3	4
3	$-0.9472e$	2.0891	1.0953	1.2631	$-0.0772e$
	$-2.0528e$	0.4284	-0.2949	-0.4924	$-0.4609e$
		-2.2275	-1.6632	-0.5679	$-1.9631e$
			-1.9158	-1.8639	
	$1.1583f$			-2.0497	$1.3647f$
	$-2.1583f$				$-0.6224f$
					$-1.9813f$
4	$1.2770e$	0.8532	1.1788	1.3187	$1.4008e$
	$-2.6103e$	-3.2223	-1.8456	-1.0616	$-1.3091e$
			-2.5613	-2.2381	$-2.2423e$
				-2.3220	
	$-1.6667f$				$-0.6323f$
					$-2.2586f$
5	$-1.6667e$	1.3538	1.5455	1.5304	$-0.8887e$
			-2.1176	-1.3746	$-2.5476e$
				-2.6033	
	$-1.6667f$				$1.5328f$
					$-2.2419f$
6	$2.5e$		2.2883	1.9778	$1.8096e$
				-1.2870	$-2.3823e$
					$-0.9818f$
7				2.7634	$-0.7636e$
					$2.2909f$
8					$3.0545e$

Tables I–III. These tables will cover all interactions of atoms $[(np)^\mu$ and $(nd)^\mu]$ in levels resulting from ground terms. In Table IV, the values of $C_2(LL)$ and $D_2(JJ)$ for ground terms of given configurations are given through atoms with $(nd)^\mu$ configurations. Mean-square radii of incomplete p shells and d shells have been calculated by use of Clementi's[25] atomic wave functions, and is given in Tables V and VI. For d shells, mean-quadratic radii are also given in Table VI, which will be used for the calculation of higher multipole interactions.

For (J_a, J_b) coupling case of like atoms in the same configurations and same terms, but with different J (different levels), the elements of matrix $\mathbf{W}_5$ have a common factor $\langle r_a^2\rangle^2$. The coefficients $D_2(J_iJ_j)D_2(J_kJ_l)$ cannot be factored out any more. Dividing out the factor $\langle r_a^2\rangle^2$ we have again a dimensionless secular determinant. If we denote the roots of determinants by $\alpha'(J_aJ_b\Omega)$, the quadrupole–quadrupole interaction energies for this case can be written in the form

$$\alpha'(J_aJ_b\Omega)\langle r_a^2\rangle^2/R^5. \qquad (3.57)$$

The values of $\alpha'(J_aJ_b\Omega)$ through configuration $(nd)^\mu$ are given in Table VII.

2. *First-Order Coulombic Energies in General for Extreme Cases*

For the interactions between atoms with $(np)^\mu$ configurations, the one nonvanishing first-order term is the quadrupole–quadrupole interaction which is proportional to R^{-5}. This case has been considered in detail above. For the case of atoms with $(nd)^\mu$ configurations, the elements of matrix $\mathbf{W}'$ have the following forms in general:

$$V_{ij}'=(W_5)_{ij}/R^5+(W_7)_{ij}/R^7+(W_9)_{ij}/R^9. \qquad (3.58)$$

For atoms with $(nf)^\mu$ configurations, more terms of higher order in R^{-1} will appear. For these cases one can obtain the first-order (electrostatic) energy by solving secular equations for given R. However, it will be seen that the expression of the interaction energy in a power series of R^{-1} is very useful for the present case. A simple method of expanding the interaction energy in power series of R^{-1} has been given in the Appendix. Here we consider only the (J_a, J_b) coupling case in which the atomic spin–orbit splitting is very large compared to the interaction energy.

For the interaction of two unlike atoms or like atoms in the same levels, we can write the first-order energy in the form

$$E^{(1)}=\alpha(J_aJ_b\Omega)D_2(J_aJ_a)D_2(J_bJ_b)\langle r_a^2\rangle\langle r_b^2\rangle/R^5$$
$$+[\beta_1D_2(J_aJ_a)D_4(J_bJ_b)\langle r_a^2\rangle\langle r_b^4\rangle+\beta_2D_4(J_aJ_a)D_2(J_bJ_b)\langle r_a^4\rangle\langle r_b^2\rangle]/R^7+\gamma/R^9+\cdots, \qquad (3.59)$$

where the first term is the quadrupole–quadrupole interaction energy, and β_1 and β_2 depend only on J_a and J_b.

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[25] E. Clementi, "Tables of Atomic Functions," a supplement of "AB Initio Computations in Atoms and Molecules," IBM J. Res. Develop. **9**, 2 (1965); J. Chem. Phys. **38**, 996 (1962); **38**, 1001 (1962); **41**, 295 (1964); **41**, 303 (1964).

TABLE II. $\alpha(J_aJ_b\Omega)$ for half-integral J and integral Ω. For like atoms in the same level, g means gerade and u means ungerade. a means that the state is positive if $d=1$, negative if $d=-1$, while b means that the state is positive if $d=-1$, negative if $d=1$.

	$J_a=1.5$	2.5	2.5	3.5	3.5
Ω	$J_b=1.5$	1.5	2.5	1.5	2.5
0	3.2*ua* −0.8*ua*	2.1294*a* −1.1673*a*	3.3883*ua* 1.3791*ua* −1.1674*ua*	1.8330*a* −1.3093*a*	2.4023*a* 0.8176*a* −1.2603*a*
	2.4*gb* 0.0*gb*	1.5162*b* −0.5540*b*	3.1756*gb* 1.3201*gb* −0.8957*gb*	1.3797*b* −0.8560*b*	1.8774*b* 1.2519*b* −1.1698*b*
1	1.2*u* −0.8*u*	2.7890 1.2582 −0.6638 −1.4592	1.6078*u* 1.1915*u* −1.1279*u*	2.0368 1.2766 −0.8143 −1.4516	3.4135 1.4845 1.1728 0.5179 −1.2131 −1.4564
	−1.6*g*		0.8655*g* −1.3369*g*		
2	−2.8*u*	0.8450 −1.4266 −1.9841	−0.2850*u* −1.7721*u*	2.7210 1.0509 −1.0342 −1.6902	1.2072 0.7810 −0.0653 −1.4696 −1.7831
	0.4*g*		1.0584*g* −1.7441*g*		
3	1.2*u*	0.8139 −2.7382	1.0190*u* −2.4333*u*	0.9052 −1.7080 −2.0777	1.1425 −0.8957 −1.9270 −2.0990
			−1.9286*g*		
4		1.6036	−2.1429*u*	1.1268 −2.6980	1.2532 −1.7071 −2.6255
			1.2857*g*		
5			2.1429*u*	1.8330	1.6386 −1.7785
6					2.4495

	$J_a=3.5$	4.5	4.5	4.5	4.5
Ω	$J_b=3.5$	1.5	2.5	3.5	4.5
0	3.7136*ua* 1.9648*ua* 0.4449*ua* −1.3233*ua*	1.7016*a* −1.3713*a*	2.1003*a* 0.5080*a* −1.3725*a*	2.6207*a* 1.5597*a* 0.2758*a* −1.4290*a*	4.0179*ua* 2.2241*ua* 1.0994*ua* 0.1723*ua* −1.5137*ua*
	3.6803*gb* 1.4663*gb* 0.9853*gb* −1.3319*gb*	1.3445*b* −1.0142*b*	1.5157*b* 1.0787*b* −1.3585*b*	2.4347*b* 1.4469*b* 0.5997*b* −1.4541*b*	4.0135*gb* 1.7894*gb* 1.4717*gb* 0.2562*gb* −1.5308*gb*
1	2.1133*u* 1.4003*u* 0.8058*u* −1.4242*u*	1.7802 1.2895 −0.9592 −1.4499	2.4833 1.4294 1.0541 0.3555 −1.2772 −1.5735	3.8253 1.8748 1.4319 1.2976 0.4679 0.1643 −1.4361 −1.5713	2.4807*u* 1.5969*u* 1.4539*u* 0.1551*u* −1.5805*u*
	1.8052*g* 0.3035*g* −1.4040*g*				2.3898*g* 0.9592*g* 0.1090*g* −1.5641*g*
2	0.7475*u* −0.1090*u* −1.6481*u*	2.0776 1.1530 −0.9858 −1.5842	3.4592 1.2968 0.8512 0.0239 −1.3636 −1.7959	1.7192 1.3810 0.7821 0.1246 −0.1419 −1.5647 −1.7958	1.3498*u* 0.5661*u* −0.0827*u* −1.7120*u*
	1.3083*g* 0.1360*g* −1.6920*g*				1.4497*g* 1.0204*g* −0.1390*g* −1.7251*g*

TABLE II. (*Continued*)

Ω	$J_a=3.5$ $J_b=3.5$	4.5 1.5	4.5 2.5	4.5 3.5	4.5 4.5
3	1.2742*u* −0.7118*u* −2.0482*u* −0.5714*g* −2.0*g*	2.6918 1.0217 −1.2850 −1.7680	1.2309 0.4452 −0.4633 −1.6305 −1.9657	1.3569 0.0911 −0.3410 −0.5574 −1.8251 −2.0399	1.4376*u* 0.2338*u* −0.5875*u* −1.9475*u* 0.0726*g* −0.4472*g* −1.9436*g*
4	−1.0351*u* −2.3553*u* 1.3333*g* −2.2857*g*	1.0457 −1.8802 −2.1381	1.2730 −1.1003 −2.0120 −2.2212	1.3906 −0.6461 −1.2428 −2.1817 −2.2212	−0.2977*u* −0.9831*u* −2.2040*u* 1.4633*g* −1.0571*g* −2.1940*g*
5	1.5487*u* −2.5582*u* −1.3333*g*	1.3575 −2.6787	1.4727 −1.5096 −2.6995	1.5207 −0.9193 −2.2384 −2.5434	1.5523*u* −1.5876*u* −2.3889*u* −0.5425*g* −2.3969*g*
6	−1.2*u* 2.0*g*	1.9817	1.9063 −1.5533	1.7952 −1.0195 −2.4334	−0.6643*u* −2.6084*u* 1.7359*g* −2.0995*g*
7	2.8*u*		2.6482	2.2733 −0.8318	2.0519*u* −2.1428*u* −0.6364*g*
8				3.0271	−0.3636*u* 2.5455*g*
9					3.2727*u*

For the case of like atoms in the same levels (J), Eq. (3.59) reduces to

$$E^{(1)}=\alpha(JJ\Omega)D_2(JJ)^2\langle r_a^2\rangle^2/R^5+\beta(JJ\Omega)\langle r_a^2\rangle\langle r_a^4\rangle/R^7+\gamma(JJ\Omega)\langle r_a^4\rangle^2/R^9+\cdots, \tag{3.60}$$

where

$$\beta(JJ\Omega)=\beta'(JJ\Omega)D_2(JJ)D_4(JJ); \qquad \gamma(JJ\Omega)=\gamma'(JJ\Omega)D_4(JJ)^2, \tag{3.61}$$

$\beta'(JJ\Omega)$ and $\gamma'(JJ\Omega)$ being dependent only on J values. It is interesting to note that the second term in (3.59) and (3.60) is the only contribution to C_7/R^7 in Eq. (2.27), since the second-order energy is a even power series in R^{-1}. The contributions to C_9/R^9 in Eq. (2.27) will come from the first-order energy [the third term in Eqs. (3.59) or (3.60)] and the leading term of third-order energy.

The interactions of two Cu ($3d^94s^2$) atoms in the level $^2D_{5/2}$ and two Ni ($3d^84s^2$) atoms in the ground level $^3F_4$ are considered as examples to see the effect of higher multipole interactions explicitly. In Table VIII, the quadrupole–quadrupole interaction energy, first-order energy approximated by 3 terms in Eq. (3.60), and correct first-order energy are tabulated for Cu–Cu and Ni–Ni interactions. The results show that the lead term [$\mathcal{O}(1/R^5)$] gives a good approximation to the first-order Coulombic interaction energy for most ranges of R of interest in the long-range calculation, although the effects of higher multipole interactions are not negligible at the relatively small values of R. The three-term approximation [Eq. (3.60)] gives good agreement with the correct first-order energy through most ranges of R considered. It is, however, expected that the effects of higher multipole interactions will be much more important for the interactions of atoms in excited configurations.[4]

Since the R^{-1} expansions of the first-order Coulombic interaction energies for atoms in ground configurations converge well, it may be useful to expand the zeroth-order wave functions in the power series of R^{-1}. To see how the correct zeroth-order wave functions can be

TABLE III. $\alpha(K_aK_b\tau)$ for half-integral τ.

τ	$K_a=1.5$ $K_b=1$	2.0 1.5	2.5 1	2.5 2	3 1.5	3 2.5
0.5	2.7459 0.0 −1.0488	2.8640 1.5505 −0.3776 −1.1684	2.1688 −0.2634 −1.2252	3.1307 1.5837 1.3039 −0.7808 −1.2126	2.0364 1.3796 −0.7137 −1.3167	3.3729 1.9280 1.2647 0.9531 −1.0826 −1.2515
1.5	0.1763 −2.7219	0.9158 −1.1952 −1.8720	2.2950 0.1310 −1.7457	1.0850 0.5024 −1.2908 −1.6382	2.7472 1.1208 −0.8702 −1.6122	1.2627 1.0101 0.2829 −1.3585 −1.5675
2.5	0.8485	0.6188 −2.7702	0.5130 −3.0076	0.9075 −2.0000 −2.1658	0.8559 −1.5872 −2.0400	1.0900 −0.6716 −1.8618 −1.9821
3.5		1.4343	1.1339	1.0674 −2.4090	0.9824 −2.7144	1.1367 −1.8203 −2.5568
4.5				1.9166	1.7321	1.4746 −1.9375
5.5						2.3146

τ	$K_a=3.5$ $K_b=1$	3.5 2	3.5 3	4 1.5	4 2.5
0.5	2.0336 −0.3590 −1.3043	2.2383 1.2994 1.0401 −1.0455 −1.3413	3.5860 2.1518 1.5243 1.1381 0.5422 −1.2688 −1.3237	1.7859 1.3376 −0.9247 −1.3782	2.3980 1.5621 1.1729 0.5731 −1.2399 −1.3961
1.5	1.9815 −0.0693 −1.5419	3.1438 1.2004 0.6326 −1.1681 −1.6178	1.5290 1.3065 0.6898 0.1504 −1.4227 −1.5726	2.0545 1.2032 −0.9019 −1.5354	3.4403 1.3389 1.0198 0.2250 −1.2942 −1.6597
2.5	2.1338 0.3314 −2.0949	1.0648 −0.1089 −1.6045 −1.8552	1.2270 −0.2060 −0.4193 −1.7766 −1.9244	2.7036 1.0224 −1.1700 −1.7355	1.2088 0.5935 −0.2963 −1.5565 −1.9049
3.5	0.7582 −3.1653	1.0820 −1.8978 −2.4706	1.2368 −1.0417 −2.1840 −2.2443	0.9721 −1.8030 −2.1092	1.2051 −1.0281 −1.9735 −2.1690
4.5	1.2961	1.4084 −2.1909	1.4081 −1.5148 −2.6146	1.2507 −2.6866	1.3657 −1.6021 −2.6692
5.5		2.1909	1.8329 −1.4549	1.9145	1.7814 −1.6535
6.5			2.6458		2.5584

TABLE III. (*Continued*)

	$K_a=4$	4.5	4.5	4.5	4.5
τ	$K_b=3.5$	1	2	3	4
0.5	3.7724	1.9802	1.9745	2.5508	3.9349
	2.3371	−0.4019	1.2453	1.7459	2.5066
	1.7212	−1.3448	0.8084	1.4283	1.9542
	1.4355		−1.2167	0.7991	1.4549
	0.7427		−1.4298	0.3207	1.2573
	0.3181			−1.3629	0.3789
	−1.3806			−1.474	0.1990
	−1.4262				−1.4765
					−1.5144
1.5	1.8557	1.9155	2.3389	3.6735	2.1330
	1.3804	−0.2057	1.2401	1.4747	1.4690
	1.1573	−1.4763	0.6064	1.3386	1.4111
	0.3999		−1.1824	0.5448	0.9072
	0.0820		−1.6213	0.0653	0.1599
	−1.4920			−1.3957	0.0314
	−1.6077			−1.6966	−1.5624
					−1.6510
2.5	1.3272	1.8831	3.1500	1.3177	1.4057
	0.3555	0.1246	1.1631	1.1658	0.7356
	−0.2062	−1.7741	0.2046	0.0686	0.3194
	−0.3264		−1.3657	−0.2742	−0.1867
	−1.7507		−1.7703	−1.5847	−0.3518
	−1.8912			−1.9328	−1.7575
					−1.8772
3.5	1.3302	2.0567	1.1390	1.3084	1.4085
	−0.6306	0.5185	−0.4389	−0.6264	−0.2489
	−1.0249	−2.3416	−1.6773	−0.7352	−0.6648
	−2.1105		−1.9836	−1.9400	−0.8618
	−2.1598			−2.1067	−2.0419
					−2.1268
4.5	1.4284	0.9342	1.2743	1.4012	1.4723
	−0.9852	−3.2697	−1.8010	−1.0449	−0.6038
	−2.2751		−2.6315	−2.2407	−1.4791
	−2.4653			−2.4062	−2.3045
					−2.3357
5.5	1.6772	1.4013	1.6647	1.6442	1.6319
	−1.1677		−2.0595	−1.2495	−0.7891
	−2.4940			−2.5876	−2.1809
					−2.5953
6.5	2.1455		2.3686	2.1051	1.9301
	−0.9966			−1.1516	−0.8162
					−2.2807
7.5	2.9245			2.8604	2.4185
					−0.5741
8.5					3.1618

written in a power series of R^{-1}, a calculation has been made for $\mathrm{O}_g{}^+$ states of Cu–Cu system in which both Cu atoms are in the configuration $3d^94s^2$ and level $^2D_{5/2}$. Let

$$\chi(M)\equiv\chi(JJg\Omega M). \qquad (3.62)$$

If the perturbation V' is approximated by

$$V'\cong W_5/R^5, \qquad (3.63)$$

the zeroth-order wave functions are

$$\begin{aligned}
\psi_1{}^{(0,0)}&=0.8521\chi(5/2)+0.4905\chi(3/2)+0.1828\chi(1/2),\\
\psi_2{}^{(0,0)}&=-0.1932\chi(5/2)+0.0299\chi(3/2)+0.9807\chi(1/2),\\
\psi_3{}^{(0,0)}&=0.4865\chi(5/2)-0.8709\chi(3/2)+0.0693\chi(1/2).
\end{aligned} \qquad (3.64)$$

When we take the correct perturbation V' for this system,

$$V'=W_5/R^5+W_7/R^7+W_9/R^9, \qquad (3.65)$$

we can obtain the zeroth-order wave functions in power series of R^{-1} by the method discussed in the Appendix, and they are found to be

$$\psi_1^{(0)}=\psi_1^{(0,0)}+\frac{\langle r^4\rangle\langle r^2\rangle}{R^2}[0.6235\psi_2^{(0,0)}+0.1990\psi_3^{(0,0)}]+\frac{(\langle r^4\rangle/\langle r^2\rangle)^2}{R^4}[-0.2141\psi_1^{(0,0)}+4.163\psi_2^{(0,0)}-0.4136\psi_3^{(0,0)}]+\cdots,$$

$$\psi_2^{(0)}=\psi_2^{(0,0)}+\frac{\langle r^4\rangle/\langle r^2\rangle}{R^2}[-0.6235\psi_1^{(0,0)}-0.9617\psi_3^{(0,0)}]$$
$$+\frac{(\langle r^4\rangle/\langle r^2\rangle)^2}{R^4}[-5.086\psi_1^{(0,0)}-0.6568\psi_2^{(0,0)}+0.4400\psi_3^{(0,0)}]+\cdots,$$

$$\psi_3^{(0)}=\psi_3^{(0,0)}+\frac{\langle r^4\rangle/\langle r^2\rangle}{R^2}[-0.1990\psi_1^{(0,0)}+0.9617\psi_2^{(0,0)}]$$
$$+\frac{(\langle r^4\rangle/\langle r^2\rangle)^2}{R^4}[0.6206\psi_1^{(0,0)}+0.1838\psi_2^{(0,0)}-0.4822\psi_3^{(0,0)}]+\cdots. \quad (3.66)$$

3. Intermediate Coupling Cases

When the atomic spin–orbit splitting is of the same order of magnitude of the interaction energy, a transition region between (J_a, J_b) and (Λ, S) couplings may exist. At this region, the (Λ, S) coupling scheme is poor since the perturbation $H_{l\cdot s}(p)$, $p=a$, b, which is the same order of magnitude of V, is neglected. In the (J_a, J_b) coupling scheme, potential energy curves with the same symmetry may cross each other. Therefore, one way to consider the transition region is to apply the almost degenerate perturbation theory.[7a]

TABLE IV. Coefficients $C_2(LL)$ and $D_2(JJ)$ for ground terms. For the shells which are complete except for ϵ missing electrons, $C_2(LL)$ and $D_2(JJ)$ have the opposite sign of those for shells which have ϵ electrons.

Configuration	Level	$C_2(LL)$	$D_2(JJ)$
np	$^2P_{1/2}$	−0.63246	0.0
	$^2P_{3/2}$		−0.44721
np^2	$^3P_0$	0.63246	0.0
	$^3P_1$		−0.31623
	$^3P_2$		0.37417
nd	$^2D_{3/2}$	−0.53452	−0.44721
	$^2D_{5/2}$		−0.47809
nd^2	$^3F_2$	−0.22131	−0.18326
	$^3F_3$		−0.16599
	$^3F_4$		−0.20022
nd^3	$^4F_{3/2}$	0.22131	0.15333
	$^4F_{5/2}$		0.11269
	$^4F_{7/2}$		0.13941
	$^4F_{9/2}$		0.19343
nd^4	$^5D_0$	0.53452	0.0
	$^5D_1$		−0.31623
	$^5D_2$		−0.11454
	$^5D_3$		0.11066
	$^5D_4$		0.40044

In this approach, we take the zeroth-order Hamiltonian H_0 as

$$H_0=H'(a)+H'(b), \quad (3.67)$$

where $H'(p)$ is defined by Eq. (2.3). We take as the approximate atomic wave functions the $\phi(SLJM)$ in the $SLJM$ scheme. If we now assume the Lande interval rule, the atomic energy interval between levels differing by unity in their J values is[26]

$$\epsilon_J-\epsilon_{J-1}=J\zeta(\gamma SL), \quad (3.68)$$

where $\zeta(\gamma SL)$ is the spin–orbit parameter. The parameter has been calculated by Blume, Watson, and Freeman[11] for some atoms of interest. Experimental values of atomic energy level intervals are given in the table of Moore.[27] Thus we can obtain the relative zeroth-order energy of the system of two interacting atoms. If we now apply the almost-degenerate perturbation theory for the set of all functions $\chi(J_aJ_b\Omega M_a)$ arising from all atomic states in given terms, the secular equation will have the following form in general[7a]:

$$\begin{vmatrix} E_1^{(0)}+V_{11}'-E, & V_{12}', & \cdots \\ V_{21}', & E_2^{(0)}+V_{22}'-E, & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}=0, \quad (3.69)$$

where $E_i^{(0)}$ are the relative zeroth-order energies and V_{ij}' will have the form in general

$$V_{ij}'=(W_5)_{ij}/R^5+(W_7)_{ij}/R^7+(W_9)_{ij}/R^7+\cdots. \quad (3.70)$$

Since $E_i^{(0)}$ are of the same order of magnitude of V_{ij}', fast converging power series of E in R^{-1} are no more possible here. The secular equation should be solved for values of R.

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[26] Reference 19, pp. 194–195.

[27] C. E. Moore, *Atomic Energy Levels* [National Bureau of Standards, Washington, D. C., Circular 467, Vol. I (1949), Vol. II (1958), Vol. III (1958)].

It should be noticed here that this problem can be solved by a different approach. We take the zeroth-order Hamiltonian defined by Eq. (2.1) and apply a new perturbation

$$H'=V'+H_{l\cdot s}(a)+H_{l\cdot s}(b). \tag{3.71}$$

Here we can apply a straightforward degenerate perturbation theory to the degenerate system which is described by $\chi(S\Sigma\Lambda M_L{}^a)$ defined in Sec. IIIB2. If we now transform[28] the set $\chi(S\Sigma\Lambda M_L{}^a)$ into the set $\chi(J_aJ_b\Omega M)$ defined in Sec. IIIB1, the matrix $[H_{l\cdot s}(a)+H_{l\cdot s}(b)]$ is diagonal in the transformed representation and the matrix $\mathbf{V}'$ will be the same as the matrix $\mathbf{V}'$ in Eq. (3.69). Thus we obtain essentially equivalent secular determinants in both methods considered. In fact, the latter method has been used by Fontana[5b] for the interaction of two alkali atoms in the excited states. We will call this *the intermediate coupling.*

To see which coupling scheme is applicable to the various ranges of R for different systems, we have calculated some potential energy curves of the systems, B–B and C–O. All atoms are assumed to be in the ground terms. In Fig. 1 we have plotted the energy curve of $^1\Pi_g$ and $^3\Pi_u$ states of B_2 in the (Λ, S) coupling, and the corresponding energy curves of $0_u{}^-$, 1_u, $0_u{}^+$, 1_g, and 2_u states in the intermediate and (J_a, J_b) couplings. It is seen that the curves in the intermediate coupling merge into $\{^1\Pi_g, {}^3\Pi_u\}$ curve at small R, and they approach asymptotically the curves in the (J_a, J_b) coupling at large R. In Fig. 2, we have plotted the

Table V. Mean-square radii of incomplete p shells of the first- and second-row atoms. Clementi's[25] wave function are used. Quantities are in atomic units.

Element	Term	$\langle r^2\rangle$ $(a_0{}^2)$
B$(2p)$	^2P	6.1418
C$(2p^2)$	^3P	3.7483
	^1D	4.0448
N$(2p^3)$	^2D	2.7060
	^2P	2.8230
O$(2p^4)$	^3P	1.9741
	^1D	2.0289
F$(2p^5)$	^2P	1.5438
Al$(3p)$	^2P	13.9552
Si$(3p^2)$	^3P	8.9811
	^1D	9.5526
P$(3p^3)$	^2D	6.6961
	^2P	6.9221
S$(3p^4)$	^3P	5.0661
	^1D	5.1676
Cl$(3p^5)$	^2P	4.0602

Table VI. Mean-square and mean-quadratic radii of incomplete shells of the third-row atoms. Clementi's[25] wave functions are used. All quantities are in atomic units.

Element	Term	Orbital	$\langle r^2\rangle$ $(a_0{}^2)$	$\langle r^4\rangle$ $(a_0{}^4)$
Sc$(3d4s^2)$	^2D	$3d$	3.6562	34.1613
Ti$(3d^24s^2)$	^3F	$3d$	2.7436	18.5903
V$(3d^34s^2)$	^4F	$3d$	2.2553	12.6906
Cr$(3d^44s^2)$	^5D	$3d$	1.9224	9.4338
Mn$(3d^54s^2)$	^6S	$3d$	1.6470	6.8570
Fe$(3d^64s^2)$	^5D	$3d$	1.4948	5.7932
Co$(3d^74s^2)$	^4F	$3d$	1.3450	4.7408
Ni$(3d^84s^2)$	^3F	$3d$	1.2198	3.9967
Cu$(3d^94s^2)$	^2D	$3d$	1.1058	3.2853
Ga$(4p^1)$	^2P	$4p$	13.8348	
Ge$(4p^2)$	^3P	$4p$	9.6466	
As$(4p^3)$	^4S	$4p$	7.3699	
Se$(4p^4)$	^3P	$4p$	6.1821	
Br$(4p^5)$	^2P	$4p$	5.2216	

Table VII. $\alpha'(J_aJ_b\Omega)$ for like atoms in the same configurations and same term, but with different J.

	(np), $(np)^5$; ^2P	$(np)^2$ $(np)^4$;	^3P	(nd), $(nd)^9$; ^2D
	$J_a=1.5$	$J_a=2.$	2.	$J_a=2.5$
	J_b 0.5	$J_b=0.$	1.	$J_b=1.5$
$0_g{}^+$	0.96	0.48	0.72	0.5916 −0.0985
$0_g{}^-$	0.0		0.0499 −0.7699	0.3435 −0.2619
$0_u{}^-$	0.0		0.5299 −0.2899	0.3537 −0.0239
$0_u{}^+$	−0.96	−0.48	−0.48	0.3220 −0.4036
1_g	0.0 −0.64	−0.32	0.0742 −0.1942 −0.48	0.5852 0.2516 −0.0582 −0.4325
1_u	0.64 0.00	0.32	0.6801 0.0696 −0.3897	0.6087 0.3176 −0.1439 −0.3056
2_g	0.16	0.08	0.84 0.12	0.2681 −0.3186 −0.4034
2_u	−0.16	−0.08	0.12 −0.48	0.1117 −0.2203 −0.5347
3_g			−0.36	0.0748 −0.6952
3_u			0.12	0.2884 −0.4908
4_g				0.4408
4_u				0.2449

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[28] Note that the set of degenerate state functions can be rearranged in any desired order and combination without changing the resulting eigenvalues. Such a regrouping of the state functions corresponds to a similarity transformation which factorizes the secular determinant in some way.

TABLE VIII. Interaction energy of the 0_g^+ states of like atoms in the ground levels of given configuration. (a) Cu–Cu interaction. (b) Ni–Ni interaction. All quantities are in atomic units.

(a) $Cu(3d^9 4S^2)^2D_{5/2}$

R	E_1	E_2	E_3
6a	1.141×10^{-4}	6.744×10^{-5}	-3.219×10^{-5}
b	1.041×10^{-4}	5.699×10^{-5}	-2.936×10^{-5}
c	1.043×10^{-4}	5.687×10^{-5}	-2.939×10^{-5}
10a	8.875×10^{-6}	3.689×10^{-6}	-2.503×10^{-6}
b	8.569×10^{-6}	3.942×10^{-6}	-2.426×10^{-6}
c	8.569×10^{-6}	3.942×10^{-6}	-2.426×10^{-6}
14a	1.650×10^{-6}	6.860×10^{-7}	-4.654×10^{-7}
b	1.620×10^{-6}	7.096×10^{-7}	-4.582×10^{-7}
c	1.620×10^{-6}	7.096×10^{-7}	-4.582×10^{-7}
18a	4.697×10^{-7}	1.952×10^{-7}	-1.325×10^{-7}
b	4.645×10^{-7}	1.993×10^{-7}	-1.312×10^{-7}
c	4.645×10^{-7}	1.993×10^{-7}	-1.312×10^{-7}
22a	1.722×10^{-7}	7.159×10^{-8}	-4.857×10^{-8}
b	1.709×10^{-7}	7.257×10^{-8}	-4.827×10^{-8}
c	1.709×10^{-7}	7.257×10^{-8}	-4.827×10^{-8}
26a	7.470×10^{-8}	3.105×10^{-8}	-2.107×10^{-8}
b	7.430×10^{-8}	3.136×10^{-8}	-2.097×10^{-8}
c	7.430×10^{-8}	3.136×10^{-8}	-2.097×10^{-8}
30a	3.652×10^{-8}	1.518×10^{-8}	-1.030×10^{-8}
b	3.638×10^{-8}	1.529×10^{-8}	-1.027×10^{-8}
c	3.638×10^{-8}	1.529×10^{-8}	-1.027×10^{-8}

(b) $Ni(3d^8 4S^2)^3F_4$

R	E_1	E_2	E_3	E_4	E_5
6a	2.971×10^{-5}	1.623×10^{-5}	1.111×10^{-5}	4.423×10^{-6}	-1.109×10^{-5}
b	5.467×10^{-5}	7.305×10^{-6}	5.932×10^{-6}	2.192×10^{-6}	-1.267×10^{-5}
c	5.305×10^{-5}	9.256×10^{-6}	5.803×10^{-6}	2.572×10^{-6}	-1.326×10^{-5}
10a	2.310×10^{-6}	1.262×10^{-6}	8.641×10^{-7}	3.439×10^{-7}	-8.620×10^{-7}
b	2.834×10^{-6}	9.617×10^{-7}	6.734×10^{-7}	2.400×10^{-7}	-8.650×10^{-7}
c	2.821×10^{-6}	9.739×10^{-7}	6.734×10^{-7}	2.411×10^{-7}	-8.666×10^{-7}
14a	4.295×10^{-7}	2.347×10^{-7}	1.607×10^{-7}	6.395×10^{-8}	-1.603×10^{-7}
b	4.745×10^{-7}	2.048×10^{-7}	1.414×10^{-7}	5.301×10^{-8}	-1.595×10^{-7}
c	4.741×10^{-7}	2.053×10^{-7}	1.414×10^{-7}	5.303×10^{-8}	-1.595×10^{-7}
18a	1.222×10^{-7}	6.679×10^{-8}	4.573×10^{-8}	1.820×10^{-8}	-4.562×10^{-8}
b	1.297×10^{-7}	6.156×10^{-8}	4.232×10^{-8}	1.624×10^{-8}	-4.541×10^{-8}
c	1.296×10^{-7}	6.159×10^{-8}	4.232×10^{-8}	1.624×10^{-8}	-4.541×10^{-8}
22a	4.482×10^{-8}	2.449×10^{-8}	1.677×10^{-8}	6.674×10^{-9}	-1.673×10^{-8}
b	4.660×10^{-8}	2.319×10^{-8}	1.592×10^{-8}	6.183×10^{-9}	-1.666×10^{-8}
c	4.660×10^{-8}	2.320×10^{-8}	1.592×10^{-8}	6.183×10^{-9}	-1.666×10^{-8}
26a	1.944×10^{-8}	1.062×10^{-8}	7.272×10^{-9}	2.895×10^{-9}	-7.255×10^{-9}
b	1.999×10^{-8}	1.022×10^{-8}	7.008×10^{-9}	2.741×10^{-9}	-7.234×10^{-9}
c	1.999×10^{-8}	1.022×10^{-8}	7.008×10^{-9}	2.741×10^{-9}	-7.234×10^{-9}
30a	9.506×10^{-9}	5.194×10^{-9}	3.556×10^{-9}	1.415×10^{-9}	-3.547×10^{-9}
b	9.705×10^{-9}	5.045×10^{-9}	3.458×10^{-9}	1.358×10^{-9}	-3.539×10^{-9}
c	9.705×10^{-9}	5.045×10^{-9}	3.458×10^{-9}	1.358×10^{-9}	-3.539×10^{-9}

[a] Quadrupole–quadrupole interaction energy. [b] 3-term approximation [Eq. (3.60)]. [c] Exact first-order energy.

energy curve of $^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$ states of CO in the (Λ, S) coupling and the corresponding energy curves of 0^+, 2, 1, 0^+, 1, and 0^- states in the intermediate and (J_a, J_b) couplings. From Fig. 2, we can see a similar trend as the case of B_2, but the range of R, where the (Λ, S) coupling is applicable, is quite shortened. In Fig. 3, there is shown for the case B_2 (both B atoms in the ground ^2P) a probable correlation[29] diagram of the states in (J_a, J_b) coupling at larger R and the states in (Λ, S) coupling at smaller R. It should be noticed here that correlations for some higher states are not uniquely determined. It is also noted that at large R the lowest

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[29] For the correlation of atomic J values and molecular quantum numbers, see R. S. Mulliken, Phys. Rev. **36**, 1440 (1930).

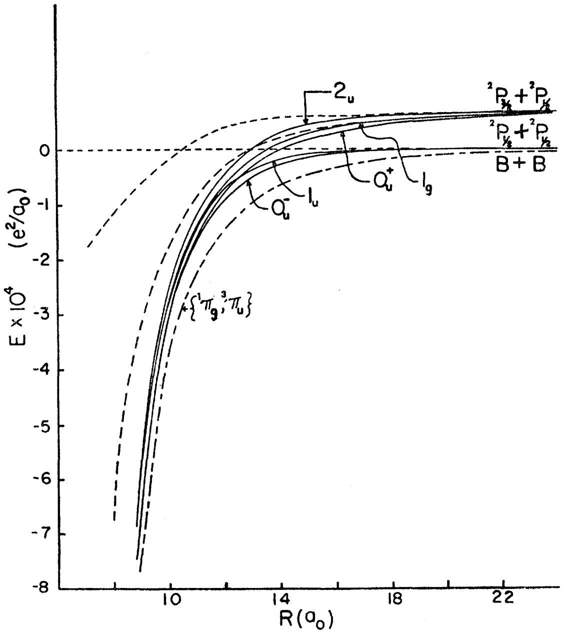


FIG. 1. Some energy curves of B_2 in the first-order approximation. Both of the separated B atoms are in the ground ^2P term. The 0_u^+, 2_u, and 1_g curves have the spin–orbit energy of the two atoms (with $\zeta = 4.438 \times 10^{-5}\, e^2/a_0$)[16b] included. –·–·– represents the curves in (Λ, S) coupling, —— those in intermediate coupling, and - - - - those in (J_a, J_b) coupling.

states are $\{{}^1\Pi_g, {}^3\Pi_u\}$, while the ground state near the equilibrium distance R_e is $^3\Sigma_g^-$. In Fig. 4, the correlations of some lower states of CO is shown.

Also, to see in what range of R strict (J_a, J_b) coupling is applicable, we have plotted the energy curves in (J_a, J_b) and intermediate couplings for the states 0_u^- of B_2 in Fig. 5(a), and for the states 0^+ of CO in Fig. 5(b). It is seen from Fig. 5 that (J_a, J_b) coupling is applicable at $R \gtrsim 16a_0$ for B_2 and at $R \gtrsim 10a_0$ for CO.

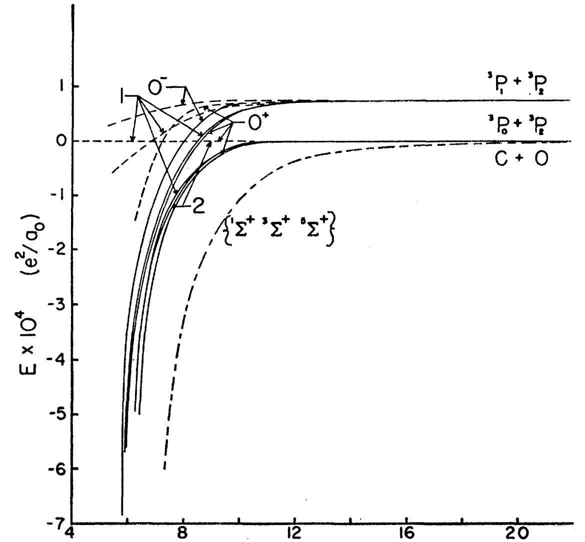


FIG. 2. Some energy curves of CO in the first-order approximation. Both of the separated atoms C and O are in the ground ^3P terms. The energy curves of the states arising from $C(^3P_1) + O(^3P_2)$ have the spin–orbit energy[27] of atoms included. –·–·– represents the curves in (Λ, S) coupling, —— those in intermediate coupling, and - - - - those in (J_a, J_b) coupling.

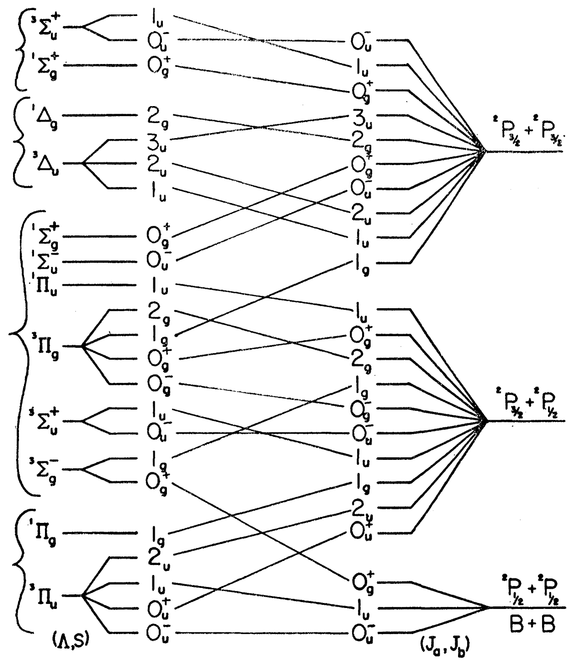


FIG. 3. A probable correlation diagram for transition from (J_a, J_b) to (Λ, S) coupling for the molecular states arising from $B(^2P) + B(^2P)$ in the first-order approximation at large R.

From the consideration of the order of magnitude of the atomic spin–orbit splittings[11,27] and interaction energies, we may conclude that, when atoms are in the ground terms, (Λ, S) coupling and intermediate coupling may have important role for the interaction between B, C, O, Al, Si, and Sc atoms. For other cases, (J_a, J_b) coupling scheme will give satisfactory results for most range of R of interest in long-range interaction.

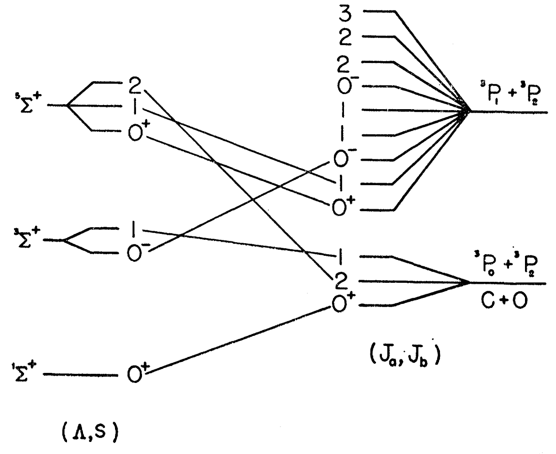
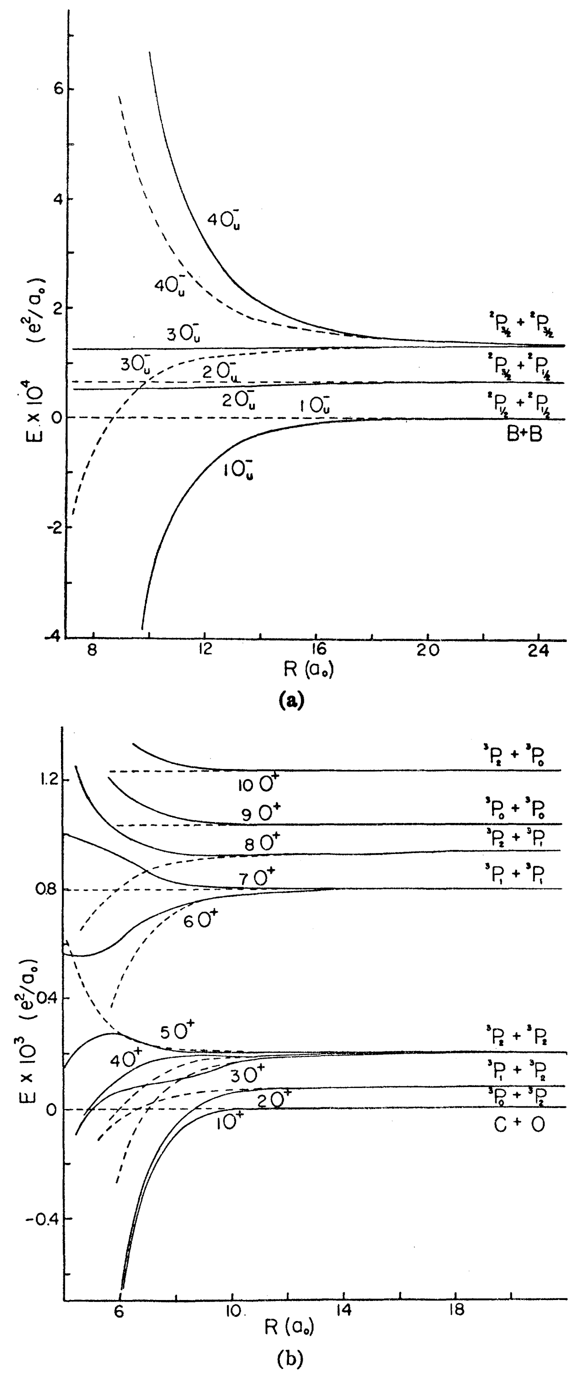


FIG. 4. Transition from (J_a, J_b) to (Λ, S) coupling for some lower molecular states arising from $C(^3P) + O(^3P)$ in the first-order approximation at large R.



(a)

(b)

FIG. 5. (a) 0_u^+ states of B_2 arising from B (^2P)+B (^2P). —— represents the energy curves in intermediate coupling and ---- those in (J_a, J_b) coupling. (b) 0^+ states of CO arising from C(^3P)+O(^3P).

D. Interatomic Forces from Predissociation Data

With a recent renewal of interest in the experimental determination of long-range interatomic forces and their comparison with theory, the most direct route has been via absolute cross sections for elastic scattering of atomic beams at thermal energies.[30] Another substantial source of relevent information is existing predissociation data.[31]

For any potential $U(R)$ with an attractive well, the effective potential $U_j(R)$ is given by

$$U_j(R)=U(R)+F[R,j(j+1)] \tag{3.72}$$

where

$$F[R,j(j+1)]=j(j+1)/2\mu R^2. \tag{3.73}$$

Here μ is the reduced mass and j is the rotational quantum number of a diatomic molecule of interest. In Hund's case (b) j is replaced by K which gives the total angular momentum apart from spin.[32] If R_j is the value of R at the effective potential maximum for the value of j, we have

$$\{[\partial U(R)/\partial R]+(\partial F/\partial R)\}_{R=R_j}=0. \tag{3.74}$$

Let us consider now the differential dU_j

$$\begin{aligned} dU_j&=\frac{\partial U_j}{\partial R}\,dR+\frac{\partial U_j}{\partial[j(j+1)]}\,d[j(j+1)] \\ &=\left[\frac{\partial U(R)}{\partial R}+\frac{\partial F}{\partial R}\right]dR+\frac{\partial F}{\partial[j(j+1)]}\,d[j(j+1)]. \end{aligned} \tag{3.75}$$

From Eqs. (3.74) and (3.75), we obtain

$$dU_j/d[j(j+1)]=\{\partial F/\partial[j(j+1)]\}_{R=R_j}, \tag{3.76}$$

and by use of Eq. (3.73) we get[33]

$$dU_j/d[j(j+1)]=(2\mu R_j^2)^{-1}. \tag{3.77}$$

A curve between the energy of the effective potential maximum and $j(j+1)$ is the limiting curve of dissociation (LCD) developed by Schmid and Gerö.[33] Extrapolating the breaking-off data to $j(j+1)=0$, we obtain dissociation energy D_0.

By use of Eqs. (3.72), (3.73), and (3.77) we obtain

$$\begin{aligned} U(R_j)&=U_j-[j(j+1)/2\mu R_j^2] \\ &=U_j-\{dU_j/d[j(j+1)]\}. \end{aligned} \tag{3.78}$$

Hence if we know LCD, then we can obtain information about long-range interatomic force since R_j is usually larger than the equilibrium distance R_e.

Recently the explicit relationships needed to make use of LCD for the determination of long-range interatomic forces has been developed by Bernstein.[31] For a potential whose long-range behavior can be expressed by $U(R)\sim -C_n'R^{-n}$, the effective potential may be

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[30] See, e.g., R. B. Bernstein in *Atomic Collision Processes*, M. R. C. McDowell, Ed. (North-Holland Publ. Co., Amsterdam, 1964), p. 895; H. Pauly and J. P. Toennies, in *Advances in Atomic and Molecular Physics*, D. R. Bates and I. Esterman, Eds. (Academic Press Inc., New York, 1965), Vol. 1, p. 201; E. W. Rothe and R. H. Neynaber, J. Chem. Phys. **43**, 4177 (1965).

[31] R. B. Bernstein, Phys. Rev. Letters **16**, 385 (1966).

[32] See Ref. 18f, p. 221.

[33] R. Schmid and L. Gerö, Z. Physik **104**, 724 (1937).

approximated, for the case where $R_j \gtrsim 1.5R_e$, by

$$U_j(R) \cong -C_n'R^{-n} + [j(j+1)/2\mu R^2], \quad (3.79)$$

so that from Eq. (3.74) we obtain

$$R_j \cong [n\mu C_n'/j(j+1)]^{1/(n-2)}. \quad (3.80)$$

Using Eqs. (3.79), and (3.80), we now obtain an explicit expression for the LCD; i.e., for E_{LCD} in atomic units:

$$E_{\mathrm{LCD}} = E_0 + U_j(R_j)$$
$$\cong E_0 + S_n[j(j+1)]^{n/(n-2)}, \quad (3.81)$$

where

$$S_n = (n-2)[1/(n\mu)^n C_n'^2]^{1/(n-2)}, \quad (3.82)$$

and E_0 is the term corresponding to the dissociation limit. For the case of $n=6$ for which E_{LCD} is linear in $[j(j+1)]^{3/2}$, the LCD data of the $x\ {}^2\Sigma^+$ state of HgH and HgD, and the $C\ {}^3\Pi_u$ state of N_2 have been used[31] successfully for the determination of C_6'.

Another example[33a] is the predissociation of the $b\ {}^3\Sigma^+$ state of CO [34] (which has been also considered by Bernstein,[31] but not fully); this state dissociates to C $({}^3P)$ and O $({}^3P)$. We make use of the following breaking-off data: for $v=0$, $K(K+1)=3173$ at 90142 cm^{-1} (see Ref. 34a) and for $v=1$, $K(K+1)=1930$ at 89820 cm^{-1} (see Ref. 34b). Here v is the vibrational quantum number. If we assume $U(R) \cong -C_5'R^{-5}$, E_{LCD} is linear in $[j(j+1)]^{5/3}$, and we obtain $S_5 = 8.3\times10^{-4}$ cm^{-1}, $C_5' = 1.5\times10^{-51}$ erg·cm$^5 = 8.0\ e^2\cdot a_0^4$, $R_j \cong 7a_0$ at $j=43$, and $D_0 = 89570$ cm^{-1}. If we now assume $U(R) \cong -C_6'R^{-6}$, we obtain $S_6 = 3.4\times10^{-3}$ cm^{-1}, $C_6' = 3.7\times10^{-59}$ erg·cm$^6 = 39\ e^2\cdot a_0^5$, and $D_0 = 89530$ cm^{-1}. The recommended value of dissociation energy[35] D_0 is 89620 ± 20 cm^{-1}, which is closer to the case of $n=5$. Hence we might conclude that $-C_5'R^5$ is a better approximation to $U(R)$ for the state $b\ {}^3\Sigma^+$ of CO.

If we neglect atomic spin–orbit splittings [(Λ, S) coupling], we have the following states of CO arising from $\mathrm{C}({}^3P)+\mathrm{O}({}^3P)$ in the first-order long-range approximation: the lowest level has the states ${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^5\Sigma^+$ with $C_5' = 1.927\times10^{-51}$ erg·cm$^5 = 10.65\ e^2\cdot a_0^4$; the next has the states ${}^1\Delta$, ${}^3\Delta$, ${}^5\Delta$ with $C_5' = 1.775\ e^2\cdot a_0^4$; the states ${}^1\Sigma^-$, ${}^3\Sigma^-$, ${}^5\Sigma^-$, ${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^5\Sigma^+$, ${}^1\Pi$, ${}^3\Pi$, ${}^5\Pi$ have $C_5'=0$; and the states ${}^1\Pi$, ${}^2\Pi$, ${}^3\Pi$ are repulsive with $C_5' = -7.100\ e^2\cdot a_0^4$. If the second-order perturbation does not reverse the order of energy levels for two ${}^3\Sigma^+$ states at large R (this is unlikely since the second-order perturbation energy is expected to be almost the same for both ${}^3\Sigma^+$ states; see Sec. IVA), we have to correlate the lower $a'\ {}^3\Sigma^+$ state to the lower ${}^3\Sigma^+$ state at large R and $b\ {}^3\Sigma^+$ to the upper ${}^3\Sigma^+$ state[36] at large R. This follows from the noncrossing rule.[35] Hence in (Λ, S) coupling the $b\ {}^3\Sigma^+$ state has no quadrupole–quadrupole interaction energy. However, if we include the effect of atomic spin–orbit splittings (intermediate coupling), $b\ {}^3\Sigma^+$ state splits to the states 0^-, 1 and there appear nonvanishing first-order energies [cf. Figs. 2 and 5(b).]. This may support the above result of the analysis of the predissociation data for the $b\ {}^3\Sigma^+$ state of CO. It is, however, noted that it is not possible to find fast-converging R^{-1} series of the interaction energy in some range of R in the intermediate coupling. It is also noted that the second-order dispersion energy may not be negligible compared to the first-order energy at $R \cong 7a_0$ which is in the range of R of interest (see Sec. IVA).

IV. SECOND-ORDER COULOMBIC INTERACTION AND MAGNETIC INTERACTION OF TWO ATOMS

A. Second-Order Coulombic Interaction of Two Atoms

In this section we consider the leading term $[\mathcal{O}(1/R^6)]$ of the second-order Coulombic interaction energy between two atoms in degenerate states. This dispersion energy will be compared with the first-order quadrupole–quadrupole interaction energy. Since the dispersion energy may be more important in the relatively shorter internuclear separation for the system with nonvanishing first-order interaction energy, we assume (Λ, S) coupling for the system of two interacting atoms.

For the calculation of dispersion energies, some accurate methods are available, which have been applied successfully for the interaction between atoms in nondegenerate states. One method is that, by making use of the identity[37]

$$(a+b)^{-1} = \frac{2}{\pi}\int_0^\infty \frac{ab}{(a^2+\omega^2)(b^2+\omega^2)}\,d\omega, \quad (4.1)$$

it is possible to reduce the original many-center problem to a number of single-center problems. A formal expression has been derived by Mavroyannis and Stephen[8b] and by McLachlan[38] which relates the leading term of the dispersion energy of two atoms to the electric dipole atomic polarizabilities, evaluated at imaginary frequencies.[39] This method has been applied for the

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[33a] *Note added in proof.* The predissociation data of Se_2 has been used to determine C_5' for Se_2 by Byrne, Richards, and Horsley [Mol. Phys. **12**, 273 (1967)]. Also see T. Y. Chang, Mol. Phys. (to be published).

[34] (a) L. Gerö, Z. Physik **95**, 747 (1935); (b) R. Schmid and L. Gerö, Z. Physik **96**, 198 (1935); (c) L. Gerö, Z. Physik **101**, 311 (1936); (d) R. Schmid, Physik. Z. **37**, 55 (1936).

[35] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Dover Publications, Inc., New York, 1950).

[36] Note that Bernstein[31] correlated $b\ {}^3\Sigma^+$ state to the lower ${}^3\Sigma^+$ state at long range R and he used only one breaking-off data[34b] $(v=1)$ for the determination of C_5'.

[37] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958), Chap. XII; *Electrodynamics of Continuous Media* (Pergamon Press, Inc., New York, 1960), Chap. IX.

[38] A. D. McLachlan, Proc. Roy. Soc. (London) **A271**, 387 (1962).

[39] For the calculation of frequency-dependent polarizabilities, see (a) M. Karplus and H. J. Kolker, J. Chem. Phys. **39**, 2997 (1963); (b) Y. M. Chan and A. Dalgarno, Proc. Phys. Soc. (London) **85**, 1455 (1965).

interactions of nondegenerate atoms.[40] The other method is to apply variational method by choosing appropriate perturbed wave functions.[41] Although these methods could be generalized to degenerate atoms, it will be much more complicated for these cases. Since we are interested in the order of magnitude of dispersion energies in the present work, we adopt a simple approximate method.

We want to calculate C_6 in Eq. (2.27). In the case of (Λ, S) coupling for the system of two interacting degenerate atoms, the zeroth-order wave functions can be written in the form

$$\psi_i^{(0)}=\sum_{M_L} C(M_L)\chi(M_L), \tag{4.2}$$

where $\chi(M_L)\equiv\chi(S\Sigma\Lambda M_L)$ or $\chi(S\Sigma\Lambda_u^g M_L)$ has been defined in Sec. IIIB2. Since $\chi(M_L)$ is a linear combination of the products of atomic wave functions, the C_6 coefficient can be written in the form [cf. Eqs. (2.9) and (2.26)]

$$C_6=-\sum_{k_a'\neq k_a,k_b'\neq k_b}\ \sum_{M_a',M_b'} \frac{\left|\sum_{M_a,M_b}\langle\phi_a(k_aM_a)\phi_b(k_bM_b)|\,V_3\,|\phi_a(k_a'M_a')\phi_b(k_b'M_b')\rangle\langle\phi_a(k_aM_a)\phi_b(k_bM_b)|\,\psi_i^{(0)}\rangle\right|^2}{\Delta\epsilon_a(k_a')+\Delta\epsilon_b(k_b')}, \tag{4.3}$$

where

$$\begin{aligned}\Delta\epsilon_a(k_a')&=\epsilon_a(k_a')-\epsilon_a(k_a),\\ \Delta\epsilon_b(k_b')&=\epsilon_b(k_b')-\epsilon_b(k_b),\end{aligned} \tag{4.4}$$

and

$$\begin{aligned}V_3&=\mathbf{r}(a)\cdot\mathbf{r}(b)-3Z(a)Z(b)\\ &=X(a)X(b)+Y(a)Y(b)-2Z(a)Z(b).\end{aligned} \tag{4.5}$$

$-\mathbf{r}(a)$ is the electric dipole moment operator of atom a. The state of an isolated atom a has been characterized by the magnetic quantum number M_a and the symbolic quantum number k_a for the set of remaining quantum numbers, and similarly for atom b. It is obvious, from Eq. (4.3), that C_6 is different for different molecular states which arise from the same configuration and term of isolated molecules. Since we are interested in the order of magnitude of C_6, the expression for C_6 will be averaged over the magnetic quantum numbers of both atoms to derive an approximate formula. Then we obtain the following expression:

$$\begin{aligned}\bar{C}_6=(2L_a+1)^{-1}\cdot(2L_b+1)^{-1}\sum_{k_a'\neq k_a,k_b'\neq k_b}\ \sum_{M_a',M_b'}\ \sum_{M_a,M_b}\times\{&|\langle\phi_a(k_aM_a)|\,X\,|\phi_a(k_a'M_a')\rangle|^2\,|\langle\phi_b(k_bM_b)|\,X\,|\phi_b(k_b'M_b')\rangle|^2\\ &+|\langle\phi_a(k_aM_a)|\,Y\,|\phi_a(k_a'M_a')\rangle|^2\,|\langle\phi_b(k_bM_b)|\,Y\,|\phi_b(k_b'M_b')\rangle|^2+4\,|\langle\phi_a(k_aM_a)|\,Z\,|\phi_a(k_a'M_a')\rangle|^2\\ &\times|\langle\phi_b(k_bM_b)|\,Z\,|\phi_b(k_b'M_b')\rangle|^2\}/\{\Delta\epsilon_a(k_a')+\Delta\epsilon_b(k_b')\}.\end{aligned} \tag{4.6}$$

Here, the fact that the cross terms such as

$$\langle\phi_a(k_aM_a)|\,X\,|\phi_a(k_a'M_a')\rangle\langle\phi_a(k_aM_a)|\,Y\,|\phi_a(k_a'M_a')\rangle$$

vanish has been used. If we now define the average quantum-mechanical oscillator strength[42]

$$\bar{f}(k,k')=(2L_k+1)^{-1}\sum_{M,M'} f(kM,k'M'), \tag{4.7}$$

where

$$f(kM,k'M')=-\tfrac{2}{3}\Delta\epsilon(k')\,|\langle\phi(kM)|\,\mathbf{r}\,|\phi(k'M')\rangle|^2, \tag{4.8}$$

and $2L_k+1$ is the degeneracy of the kth level of an atom, one can show that[43]

$$\bar{f}^{(x)}(k,k')=\bar{f}^{(y)}(k,k')=\bar{f}^{(z)}(k,k')=\tfrac{1}{3}\bar{f}(k,k'). \tag{4.9}$$

Here $\bar{f}^{(x)}(k,k')$ is defined by Eqs. (4.7) and (4.8) if we replace $\mathbf{r}$ by X, and similarly for $\bar{f}^{(y)}(k,k')$ and $\bar{f}^{(z)}(k,k')$. Using Eqs. (4.7), (4.8), and (4.9), we obtain

$$\bar{C}_6=-\tfrac{3}{2}\sum_{k_a'\neq k_a,k_b'\neq k_b}\frac{\bar{f}_a(k_a,k_a')\bar{f}_b(k_b,k_b')}{\Delta\epsilon_a(k_a')\Delta\epsilon_b(k_b')[\Delta\epsilon_a(k_a')+\Delta\epsilon_b(k_b')]}. \tag{4.10}$$

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[40] For examples, see (a) M. Karplus and H. J. Kolker, J. Chem. Phys. **41**, 3955 (1964); (b) Y. M. Chan and A. Dalgarno, Mol. Phys. **9**, 349 (1965).

[41] For nice discussions, see (a) R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 113 (1937); (b) K. S. Pitzer, Advan. Chem. Phys. **2**, 59 (1959).

[42] See Ref. 1, p. 890.

[43] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

TABLE IX. Estimates for $\bar{C}_6$. $\bar{C}_6$ are estimated by Eq. (4.10) with $\Delta\bar{\epsilon}=I$ and polarizabilities estimated by Eq. (4.11). R^* is the distance of twice the sum of the atomic radii which is taken from Slater's[48] table. All quantities are in atomic units.

	R^*	I	α	$-\bar{C}_6$	$-C_5$	$\bar{C}_6/(C_5R^*)$	States
He–He		0.9033	1.248	1.055			
			(1.384)[a]	(1.456)[b]			
Ne–Ne		0.7923	2.451	3.570			
			(2.663)[a]	(6.31)[b]			
B_2	6.44	0.3049	24.79	140.5	36.22	0.602	$^1\Pi_g$, $^3\Pi_u$
C_2	5.28	0.4140	12.21	46.29	13.49	0.650	$^1\Pi_g$, $^3\Pi_u$, $^5\Pi_g$
O_2	4.52	0.5003	4.84	8.790	3.741	0.520	$^1\Pi_g$, $^3\Pi_u$, $^5\Pi_g$
CO	4.90			20.08	10.65	0.385	$^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$

[a] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) **A259**, 424 (1960).
[b] See Ref. 49.

It follows, from Eqs. (4.3) and (4.10), that, for the interactions of two atoms in the ground configuration and term, C_6 is negative and hence the London dispersion force is attractive.

If we now apply Unsöld's approximation[44] to Eq. (4.10) and introduce the average dipole polarizability[42] for atoms,

$$\bar{\alpha}=\sum_{k'\neq k}\{\bar{f}(k,k')/[\Delta\epsilon(k')]^2\}, \tag{4.11}$$

we obtain London's[45] formula for $\bar{C}_6$:

$$\bar{C}_6=-\tfrac{3}{2}[\Delta\bar{\epsilon}_a\Delta\bar{\epsilon}_b/(\Delta\bar{\epsilon}_a+\Delta\bar{\epsilon}_b)]\bar{\alpha}_a\bar{\alpha}_b. \tag{4.12}$$

Here $\Delta\bar{\epsilon}_a$ and $\Delta\bar{\epsilon}_b$ are appropriate average excitation energies for atoms a and b. It is often found that choosing the average excitation energies $\Delta\bar{\epsilon}$ equal to the first ionization potentials[46] I of the interacting atoms gives good estimates for $\bar{C}_6$. For the estimation of the atomic polarizabilities, we will employ the Buckingham's[47] formula

$$\alpha=\tfrac{4}{9}\sum_{i=1}^{n}(r^2)_i^2, \tag{4.13}$$

where

$$(r^2)_i=\langle u_i\mid r^2\mid u_i\rangle-\sum_{i'\neq i}\{\langle u_{i'}\mid x\mid u_i\rangle\langle u_i\mid x\mid u_{i'}\rangle+\langle u_{i'}\mid y\mid u_i\rangle\langle u_i\mid y\mid u_{i'}\rangle+\langle u_{i'}\mid z\mid u_i\rangle\langle u_i\mid z\mid u_{i'}\rangle\}, \tag{4.14}$$

in which u_i are atomic spin orbitals and n is the number of electrons in an atom. The necessary atomic properties $\langle u_i\mid r^2\mid u_i\rangle$ and $\langle u_i\mid r\mid u_{i'}\rangle$ for the evaluation of the polarizabilities are calculated by use of Clementi's wave function.[25] Values for $\bar{C}_6$ obtained from Eq. (4.12) with $\Delta\bar{\epsilon}_a=I_a$ and $\Delta\bar{\epsilon}_b=I_b$ are given in Table IX for the interactions of the first-row atoms. The ratio of the van der Waals energy to the quadrupole–quadrupole interaction energy, $\bar{C}_6/(C_5R^*)$ at distance R^* of twice the sum of the atomic radii which are taken from Slater's[48] table, is also given in Table IX. Estimated values for $\bar{C}_6$ for He–He and Ne–Ne interactions are smaller than accurate values[49] in magnitude (see Table IX), and hence this may be true for other systems. Hence the van der Waals dispersion energies may be of almost the same size as the quadrupole–quadrupole interaction energies at the separation R^*, although estimated values of the ratio $\bar{C}_6/(C_5R^*)$ are about 0.6. (See Table IX). Since the quadrupole–quadrupole interaction energies are proportional to $\mathcal{O}(R^{-5})$, it is, however, expected that, when the quadrupole–quadrupole interaction energies do not vanish, the first-order Coulombic interaction energy is dominant compared to higher-order Coulombic interaction energies throughout most range of R of interest in long-range interactions.

B. Magnetic Interaction of Two Atoms

The purpose of this subsection is to consider magnetic interaction energy of two atoms. The general treatment of magnetic (or relativistic) long-range interaction energies through $\mathcal{O}(\alpha^2)$ has been considered briefly in Section IIB. Here we will consider only the leading term $[\mathcal{O}(\alpha^2/R^3)]$ of magnetic interaction of two neutral atoms in degenerate states to see in what range of R magnetic interaction energies are appreciable. We also assume (J_a, J_b) coupling for the system of the two

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[44] A. Unsöld, Z. Physik **43**, 563 (1927).

[45] (a) F. London, Z. Physik. Chemie **B11**, 222 (1930); (b) Trans. Faraday Soc. **33**, 8 (1937).

[46] The experimental ionization potentials are listed by Moore.[27]

[47] R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 (1937).

[48] J. C. Slater, J. Chem. Phys. **41**, 3199 (1964).

[49] A. E. Kingston, Phys. Rev. **A135**, 1018 (1964).

interacting atoms since magnetic interactions are important in the relatively longer internuclear separation.

It has been shown by Meath[6b] that the interaction energy through $\mathcal{O}(\alpha^2/R^3)$ is identically equal to the semiclassical result for nonresonant cases. From semiclassical consideration one would expect that two atoms a and b with magnetic dipoles $\mathbf{M}(a)=-\frac{1}{2}\alpha[\mathbf{L}(a)+2\mathbf{S}(a)]$ and $\mathbf{M}(b)=-\frac{1}{2}\alpha[\mathbf{L}(b)+2\mathbf{S}(b)]$, respectively, would have a magnetic dipole–dipole interaction Hamiltonian

$$H_{\mathrm{s.c.}}{}^{\mathrm{mag}}=(1/R^3)[\mathbf{M}(a)\cdot\mathbf{M}(b)-3M_z(a)M_z(b)]. \tag{4.15}$$

This semiclassical Hamiltonian can be written alternatively in the form[6]

$$H_{\mathrm{s.c.}}{}^{\mathrm{mag}}=(\alpha^2/R^3)[\Gamma_{LL,3}+\Gamma_{SS,3}+\Gamma_{SL,3}], \tag{4.16}$$

where

$$\Gamma_{LL,3}=\sum_{m=-1}^{1}\beta_{LL,3}(m)L_1^{-m}(a)L_1^m(b);\qquad \beta_{LL,3}(0)=-\tfrac{1}{2},\qquad \beta_{LL,3}(\pm1)=-\tfrac{1}{4},$$

$$\Gamma_{SS,3}=\sum_{m=-1}^{1}\beta_{SS,3}(m)S_1^{-m}(a)S_1^m(b);\qquad \beta_{SS,3}(0)=-2,\qquad \beta_{SS,3}(\pm1)=-1,$$

$$\Gamma_{SL,3}=\sum_{m=-1}^{1}\beta_{SL,3}(m)\{1+P_{ab}\}\{L_1^{-m}(a)S_1^m(b)\};\qquad \beta_{SL,3}(0)=-1,\qquad \beta_{SL,3}(\pm1)=-\tfrac{1}{2}. \tag{4.17}$$

Here, for a tensor operator of rank 1, **A**, the irreducible spherical components, are defined in terms of the ordinary Cartesian components by

$$\begin{aligned} A_1^{+1}&=-\sqrt{2}^{-1}(A_x+iA_y)\\ A_1^0&=A_z\\ A_1^{-1}&=\sqrt{2}^{-1}(A_x-iA_y). \end{aligned} \tag{4.18}$$

The expansion coefficients $\Gamma_{\sigma,3}$ for $\sigma=LL$, SS, SL in Eq. (4.16) represent, respectively, the magnetic orbit–orbit, spin–spin, and spin–orbit dipole interactions between atoms a and b. In the multipole expansion of the generalized Breit–Pauli Hamiltonian[6a,16] the terms of $\mathcal{O}(\alpha^2/R)$ and $\mathcal{O}(\alpha^2/R^2)$ and further correction terms of $\mathcal{O}(\alpha^2/R^3)$ in addition to the terms in Eq. (4.16) appear. However, those terms do not give any contribution to the relativistic or magnetic interaction energies through $\mathcal{O}(\alpha^2/R^3)$. This has been shown by Meath[6b] by use of the explicit expression of multipole expansion of the generalized Breit–Pauli Hamiltonian and some commutation relations for tensorial operators.

In our calculation of magnetic interaction energy of $\mathcal{O}(\alpha^2/R^3)$, we assume that magnetic interaction energies are small compared to Coulombic interaction energies, and hence we can first diagonalize the Coulombic interaction operator V. The resulting eigenfunctions will have the following forms in general (cf. Secs. IIA and IIIC2):

$$\begin{aligned} \Psi_k&=\psi_k{}^{(0,0)}+\mathcal{O}(1/R^2),\\ \psi_k{}^{(0,0)}&=\sum C(M)\chi(M), \end{aligned} \tag{4.19}$$

where $\chi(M)\equiv\chi(J_aJ_b\Omega M)$ or $\chi(J_aJ_{bu}^{\,g}\Omega M)$ has been defined in Sec. IIIB. The magnetic interaction energy through $\mathcal{O}(\alpha^2/R^3)$ in our approximation is given by

$$\begin{aligned} E_k{}^{\mathrm{mag}}&=\langle\psi_k{}^{(0,0)}\mid H_{\mathrm{s.c.}}{}^{\mathrm{mag}}\mid\psi_k{}^{(0,0)}\rangle\\ &=\sum C(M)C(M')\langle\chi(M)\mid H_{\mathrm{s.c.}}{}^{\mathrm{mag}}\mid\chi(M')\rangle. \end{aligned} \tag{4.20}$$

Since $\chi(M)$ are linear combinations of functions $\varphi(J_aJ_bM_aM_b)=\phi_a(J_aM_a)\phi_b(J_bM_b)$, and $H_{\mathrm{s.c.}}{}^{\mathrm{mag}}$ is given by Eq. (4.16), we have to evaluate integral

$$\langle\varphi(J_aJ_bM_aM_b)\mid\Gamma_{\sigma,3}\mid\varphi'(J_a'J_b'M_a'M_b')\equiv\langle J_aJ_bM_aM_b\mid\Gamma_{\sigma,3}\mid J_a'J_b'M_a'M_b'\rangle,\qquad \sigma=LL,\ SS,\ SL.$$

Using the Wigner–Eckart theorem[21] and properties of the Clebsch–Gordan coefficients,[22] the integral for $\sigma=LL$ can be written as

$$\begin{aligned} \langle J_aJ_bM_aM_b\mid\Gamma_{LL,3}\mid J_a'J_b'M_a'M_b'\rangle&=\sum_{m=-1}^{1}\beta_{LL,3}(m)\langle J_aM_a\mid L_1^{-m}\mid J_a'M_a'\rangle\langle J_bM_b\mid L_1^m\mid J_b'M_b'\rangle\\ &=\sum_{m=-1}^{1}\beta_{LL,3}(m)C(J_a'1J_a;M_a',-m,M_a)\langle J_a\Vert L_1\Vert J_a'\rangle\\ &\qquad\times C(J_b'1J_b;M_b'mM_b)\langle J_b\Vert L_1\Vert J_b'\rangle\\ &=\delta(M_a+M_b,M_a'+M_b')\beta_{LL,3}(M_a-M_a')C(J_a'1J_a;M_a',M_a-M_a',M_a)\\ &\qquad\times C(J_b'1J_b;M_b',M_b-M_b',M_b)\langle J_a\Vert L_1\Vert J_a'\rangle\langle J_b\Vert L_1\Vert J_b'\rangle. \end{aligned} \tag{2.21}$$

To evaluate the reduced matrix elements $\langle J_P' \| L_1 \| J_P' \rangle$ we apply the projection theorem for first-rank tensors,[50] which gives

$$\langle J_P M_P \mid L_1{}^m \mid J_P' M_P' \rangle = \delta(J_P, J_P') \frac{\langle J_P M_P \mid J_1{}^m \mid J_P M_P' \rangle \langle J_P \| \mathbf{J}\cdot\mathbf{L} \| J_P \rangle}{J_P(J_P+1)}. \tag{4.22}$$

Since

$$\mathbf{J}\cdot\mathbf{L} = (\mathbf{L}+\mathbf{S})\cdot\mathbf{L} = \mathbf{L}^2 + \mathbf{S}\cdot\mathbf{L},$$

$$\mathbf{S}\cdot\mathbf{L} = \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2), \tag{4.23}$$

we have

$$\mathbf{J}\cdot\mathbf{L} = \tfrac{1}{2}(\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2) \tag{4.24}$$

and hence

$$\langle J_P \| \mathbf{J}\cdot\mathbf{L} \| J_P \rangle = \langle J_P M_P \mid \mathbf{J}\cdot\mathbf{L} \mid J_P M_P \rangle$$

$$= \tfrac{1}{2}[J_P(J_P+1) + L_P(L_P+1) - S_P(S_P+1)]. \tag{4.25}$$

Furthermore we have[21]

$$\langle J_P M_P \mid J_1{}^m \mid J_P M_P' \rangle = [J_P(J_P+1)]^{1/2} C(J_P 1 J_P;\, M_P' m M_P). \tag{4.26}$$

Substituting Eqs. (4.25) and (4.26) into Eq. (4.22), we obtain

$$\langle J_P M_P \mid L_1{}^m \mid J_P' M_P' \rangle = \frac{\delta(J_P, J_P') C(J_P 1 J_P;\, M_P' m M_P)[J_P(J_P+1) + L_P(L_P+1) - S_P(S_P+1)]}{2[J_P(J_P+1)]^{1/2}}. \tag{4.27}$$

On the other hand, the Wigner–Eckart theorem gives

$$\langle J_P M_P \mid L_1{}^m \mid J_P' M_P' \rangle = C(J_P' 1 J_P;\, M_P' m M_P) \langle J_P \| L_1 \| J_P' \rangle. \tag{4.28}$$

Thus we obtain from Eqs. (4.27) and (4.28)

$$\langle J_P \| L_1 \| J_P' \rangle = \delta(J_P', J_P) \frac{[(J_P(J_P+1) + L_P(L_P+1) - S_P(S_P+1)]}{2[J_P(J_P+1)]^{1/2}}. \tag{4.29}$$

Similarly we have for $\sigma = SS$ and SL

$$\langle J_a J_b M_a M_b \mid \Gamma_{SS,3} \mid J_a' J_b' M_a' M_b' \rangle = \delta(M_a + M_b,\, M_a' + M_b') \beta_{SS,3}(M_a - M_a') C(J_a' 1 J_a;\, M_a',\, M_a - M_a',\, M_a)$$

$$\times C(J_b' 1 J_b;\, M_b',\, M_b - M_b',\, M_b) \langle J_a \| S_1 \| J_a' \rangle \langle J_b \| S_1 \| J_b' \rangle, \tag{4.30}$$

$$\langle J_P \| S_1 \| J_P' \rangle = \delta(J_P, J_P') \frac{J_P(J_P+1) + S_P(S_P+1) - L_P(L_P+1)}{2[J_P(J_P+1)]^{1/2}} \tag{4.31}$$

and

$$\langle J_a J_b M_a M_b \mid \Gamma_{SL,3} \mid J_a' J_b' M_a' M_b' \rangle = \delta(M_a + M_b,\, M_a' + M_b') \beta_{SL,3}(M_a - M_a') \{1 + P_{ab}\} \{C(J_a' 1 J_a;\, M_a',\, M_a - M_a',\, M_a)$$

$$\times C(J_b' 1 J_b;\, M_b',\, M_b - M_b',\, M_b) \langle J_a \| L_1 \| J_a' \rangle \langle J_b \| S_1 \| J_b' \rangle\}. \tag{4.32}$$

To see the effect of magnetic interaction energy to interatomic force, we consider some particular systems.

O_2

The $0_g{}^+$ states of O_2 which arise from two separated oxygen atoms in the ground ${}^3P_2$ level are considered. The proper zeroth-order wavefunctions which diagonalize W_5 [see Eq. (3.2)] are

$$\psi_1{}^{(0)} = 0.7360\chi(2) + 0.5828\chi(1) + 0.3445\chi(0),$$

$$\psi_2{}^{(0)} = -0.2918\chi(2) - 0.1861\chi(1) + 0.9382\chi(0),$$

$$\psi_3{}^{(0)} = 0.5109\chi(2) - 0.7910\chi(1) + 0.0331\chi(0), \tag{4.33}$$

where $\chi(M) \equiv \chi(J_a J_b g \Omega M)$ are defined in Sec. IIIB1. The corresponding quadrupole–quadrupole interaction energies are

$$E_1{}^{\text{q.q.}} = 1.779/R^5,$$

$$E_2{}^{\text{q.q.}} = 0.8230/R^5,$$

$$E_3{}^{\text{q.q.}} = -0.2639/R^5. \tag{4.34}$$

The resulting magnetic interaction energies obtained from Eq. (4.20) are

$$E_1{}^{\text{mag}} = 4.743\alpha^2/R^3,$$

$$E_2{}^{\text{mag}} = -0.289\alpha^2/R^3,$$

$$E_3{}^{\text{mag}} = 1.1710\alpha^2/R^3. \tag{4.35}$$

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[50] See Ref. 27, p. 94.

TABLE X. Values of $E_i^{\text{mag}}/E_i^{\text{q.q.}}$ as a function of R for the 0_g^+ states of O_2 and Cu_2. Two separated O atoms are assumed to be in the ground ${}^3P_2$ level and Cu atoms in the configuration $(3d)^9(4s)^2$ and ${}^2D_{5/2}$ level. All quantities are in atomic units.

	0_g^+ states of O_2			0_g^+ states of Cu_2		
R	$i=1$	2	3	$i=1$	2	3
20	0.057	−0.008	0.095	0.106	−0.075	−0.059
30	0.128	−0.017	0.213	0.238	−0.168	−0.128
40	0.227	−0.030	0.378	0.423	−0.298	−0.227
50	0.355	−0.047	0.591	0.661	−0.466	−0.355
60	0.511	−0.067	0.851	0.951	−0.671	−0.512

Cu_2

The 0_g^+ states of Cu_2 which arise from two separated Cu atoms in the configuration $(3d)^9(4s)^2$ and level ${}^2D_{5/2}$ are considered. The proper zeroth-order wave functions which diagonalize W_5 are given by Eq. (3.64). The corresponding quadrupole–quadrupole interaction energies are

$$E_1^{\text{q.q.}}=0.8876/R^5,$$

$$E_2^{\text{q.q.}}=0.3690/R^5,$$

$$E_3^{\text{q.q.}}=-0.2503/R^5. \tag{4.36}$$

The resulting magnetic interaction energies are

$$E_1^{\text{mag}}=4.403\alpha^2/R^3,$$

$$E_2^{\text{mag}}=-1.291\alpha^2/R^3,$$

$$E_3^{\text{mag}}=0.6678\alpha^2/R^3. \tag{4.47}$$

The ratio of magnetic interaction energy E_i^{mag} to the quadrupole–quadrupole interaction energy $E_i^{\text{q.q.}}$ has been tabulated in Table X. It is shown that magnetic interaction energy is 10∼20% of the quadrupole–quadrupole interaction energy at $R=30a_0$ and 30∼50% at $R=50a_0$ for the systems considered here.

The magnetic interaction energies of $\mathcal{O}(\alpha^2/R^3)$ discussed here may be of importance in atomic scattering experiments.[51] If the quadrupole–quadrupole interaction energy vanishes and magnetic interaction energy of $\mathcal{O}(\alpha^2/R^3)$ does not, then the leading term of the Coulombic interaction energy is $\mathcal{O}(1/R^6)$, and hence the magnetic interaction energy will be of more importance.[6b] They are also important because they appear not to be retarded[52] at large intermolecular separations and therefore will sometimes be the lead term in the $1/R$ expansion of the very long-range interaction energy.

V. SUMMARY AND DISCUSSION

The most important feature of this work is the detailed analysis of the moderately long-range interaction energies of degenerate atoms for nonresonant cases.

We have constructed the symmetry-adapted molecular wave functions at large internuclear separation R in the general case. The quadrupole–quadrupole interaction energy, which has been considered previously by Knipp,[3] has been reconsidered, and much more extensive tabulation of necessary parameters and atomic properties has been made. For the third-row atoms with $(3d)^\mu(4s)^2$ configurations, we have considered higher multipole interactions in addition to the quadrupole–quadrupole interaction, and have shown that the $1/R$ series of the first-order Coulombic interaction energies converges very fast throughout the long-range region at least for atoms in the ground configuration.[53]

For intermediate coupling cases where the atomic spin–orbit splitting becomes of the same order of magnitude as the interaction energies, we considered two methods to calculate the interaction energies. If we keep (J_a, J_b) coupling through the transion region of R, we have to apply almost-degenerate perturbation theory. If we now assume (Λ, S) coupling through the transion region of R, we have to apply the generalized perturbation given by Eq. (3.71). As examples, we have considered the interactions of two boron atoms, and carbon and oxygen atoms. For B_2, it is shown that (Λ, S) coupling is applicable for $R\lesssim 10a_0$, and (J_a, J_b) coupling applicable for $R\gtrsim 16a_0$. For CO, (J_a, J_b) coupling is applicable for $R\gtrsim 10a_0$; however, the (Λ, S) coupling scheme is not accurate enough even at $R\cong 7a_0$. From the consideration of the order of magnitude of the atomic spin–orbit splittings[11,27] and interaction energies, we conclude that, when atoms are in the ground configuration, (Λ, S) coupling and intermediate coupling may be important for the interactions between B, C, O, Al, Si, and Sc atoms. For other cases, a (J_a, J_b) coupling scheme will give satisfactory results throughout the moderately long-range region.

The experimental determination of the moderately

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[51] See the discussion in W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. **44**, 3210 (1966).

[52] E. A. Power, W. J. Meath, and J. O. Hirschfelder, Phys. Rev. Letters **17**, 799 (1966).

[53] It is, however, noted that for the interaction of two hydrogen atoms in $2s$ or $2p$ state the series converges for $R>20a_0$ for some states. See Ref. 4, in particular, Table VI. Also see H. Kim and J. O. Hirschfelder, J. Chem. Phys. **46**, 4553 (1967).

long-range interatomic forces from the predissociation data has been considered. In particular, the predissociation data[34] of the $b\,^3\Sigma^+$ state of C–O has been analyzed in detail. The results seems to support the importance of the effects of atomic spin–orbit splitting at $R \cong 7a_0$.

The van der Waals dispersion energy averaged over the magnetic quantum numbers of both atoms has been estimated by the use of London's[45] formula for the interactions of first-row atoms. It has been shown that the dispersion energy is of almost the same size as the quadrupole–quadrupole interaction energy at the separation of twice the sum of the atomic radii. It is, however, expected that, when the quadrupole–quadrupole interaction energy does not vanish, the first-order interaction energy is the most important throughout the long-range region. We have also considered the leading term $\mathcal{O}(\alpha^2/R^3)$ of the magnetic interaction of two degenerate atoms and have shown that the magnetic interaction energy is $10\sim20\%$ of the quadrupole–quadrupole interaction energy at $R=30a_0$, and $30\sim50\%$ at $R=50a_0$, through the third-row atoms.

It should be pointed out that the first-order Coulombic interaction energies are zero when averaged over the original zeroth-order degenerate states.[10,6b] Therefore, the equation of state and equilibrium properties of a gas do not depend in an important way on the long-range first-order interactions. However, the long-range first-order interactions may lead to anomalously large values for the viscosity and other transport properties. This is due to the fact that the transport properties depend upon the cosine of the angle of deflection for a molecular collision, and hence only the absolute value of the interaction energy is of consequence.

For two rotating molecules the first-order quadrupole–quadrupole interaction energy does not vanish in general. This fact has been noted by London[45a] and reconsidered by Margenau.[43] It can be easily shown that for the interaction of two rigid linear dipoles the first-order energy vanishes, but the quadrupole–quadrupole interaction energy does not vanish for two linear quadrupoles. The diagonal terms of the energy of interaction of two rotating neutral molecules have in fact their dependence on orientation given by

$$(R^5)^{-1}\{J_a(J_a+1)-3M_a^2\}\{J_b(J_b+1)-3M_b^2\},$$

where J_a, M_a; J_b, M_b are the angular momentum and magnetic quantum numbers describing the rotational states of two molecules. Nondiagonal terms also appear, and hence the secular equations should be solved explicitly for an accurate treatment of the problem. Margenau,[43] however, concludes by a simple argument that the quadrupole–quadrupole interaction energies of actual simple molecules are negligible compared to the dispersion energies in the moderately long-range region. However, this may not be true for some cases such as radicals and excited molecules, and hence this first-order energy may effect the transport properties.

The first-order interactions discussed in this work may be important in determining the physical properties of substances containing large numbers of free atoms and excited molecules, such as hot gases or systems in which chemical reactions are taking place rapidly. These forces may also play a large role in the interaction and recombination of free atoms and free radicals.

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APPENDIX

Let the secular determinant in the first-order degenerate perturbation theory have the form

$$\begin{vmatrix} v_{11}-E^{(1)} & v_{12} & \cdots \\ v_{21} & v_{22}-E^{(1)} & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} = 0. \tag{A1}$$

When the matrix element v_{ij} in the secular determinant, Eq. (A1), can be expressed in the form

$$v_{ij}=a_{ij}+b_{ij}\mu+c_{ij}\mu^2+d_{ij}\mu^3+\cdots, \tag{A2}$$

where μ is a parameter, we may desire to express eigenvalues (first-order energies) and eigenfunctions (zeroth-order wave functions) in power series of μ. For the calculation of long-range intermolecular forces, μ will be $1/R$, where R is the intermolecular separation. The expressions in power series of μ can be obtained by applying the usual perturbation theory.

Let $\mathbf{U}$ be a unitary matrix such that $\bar{\mathbf{a}}=\mathbf{U}^+\mathbf{a}\mathbf{U}$ is diagonal and put

$$\bar{\mathbf{b}}=\mathbf{U}^+\mathbf{b}\mathbf{U}; \quad \bar{\mathbf{C}}=\mathbf{U}^+\mathbf{C}\mathbf{U}; \quad \bar{\mathbf{d}}=\mathbf{U}^+\mathbf{d}\mathbf{U};\cdots. \tag{A3}$$

If we now assume that for eigenvalues $E_i^{(1)}$

$$E_i^{(1)}=\alpha_i+\mu\beta_i+\mu^2\gamma_i+\mu^3\delta_i+\cdots, \tag{A4}$$

we obtain from the Rayleigh–Schrödinger perturbation theory

$$\alpha_i = \bar{a}_{ii},$$

$$\beta_i = \bar{b}_{ii},$$

$$\gamma_i = \sum_k{}' \frac{\bar{b}_{ik}\bar{b}_{ki}}{\alpha_i - \alpha_k} + \bar{c}_{ii},$$

$$\delta_i = 2\sum_k{}' \frac{\bar{b}_{ik}\bar{c}_{ki}}{\alpha_i - \alpha_k} + \sum_k{}' \sum_l{}' \frac{\bar{b}_{ik}\bar{b}_{kl}\bar{b}_{li}}{(\alpha_i - \alpha_k)(\alpha_i - \alpha_l)} - \sum_k{}' \frac{\bar{b}_{ik}\bar{b}_{ki}\bar{b}_{ii}}{(\alpha_i - \alpha_k)^2} + \bar{d}_{ii}, \quad \text{(A5)}$$

where α_i's are assumed to be nondegenerate and the primed sigmas indicate the sum over k or l but omitting $k=i$ or $l=i$. It should be noticed that the convergence of series (A4) depends on the separation between α_i's and the convergence of matrix elements v_{ij} themselves. It certainly diverges when α's are almost degenerate.

If we now assume that for the zeroth-order wave functions

$$\psi_i^{(0)} = \psi_i^{(0,0)} + \mu\psi_i^{(0,1)} + \mu^2\psi_i^{(0,2)} + \cdots, \quad \text{(A6)}$$

we have

$$\psi_i^{(0,0)} = \sum_k \chi_k U_{ki},$$

$$\psi_i^{(0,1)} = \sum_k{}' [\bar{b}_{ki}/(\alpha_i - \alpha_k)]\psi_k^{(0,0)},$$

$$\psi_i^{(0,2)} = \sum_k{}' \left[\sum_l{}' \frac{(\bar{b}_{kl} - \delta_{kl}\bar{b}_{ii})\bar{b}_{li}}{(\alpha_i - \alpha_l)(\alpha_i - \alpha_k)} + \frac{\bar{c}_{ki}}{\alpha_i - \alpha_k}\right]\psi_k^{(0,0)} - \tfrac{1}{2}\sum_l{}' \frac{\bar{b}_{il}\bar{b}_{li}}{(\alpha_i - \alpha_l)^2}\psi_i^{(0,0)}, \quad \text{(A7)}$$

where χ_k's are the original orthonormal basis set.

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Erratum: Possibilities of Observation of Nonlinear Quantum Electrodynamic Effects in Vacuum

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Page 53, first column, line 22 should read "2.7 parts in 10^8 and 5 parts in 10^6, respectively" and line 27 should read "to about 3 parts in 10^5 and 5 parts in 10^3, respectively."

Page 55, first column, lines 2 to 4 should read "g-factor anomaly of the free point electron is confirmed to an accuracy of about 1 percent.[22]"