

# Theory of Long-Range Interatomic Forces. III. First-Order Interaction Energies in the Coupled Representation\*

PETER R. FONTANA†

Sloane Physics Laboratory, Yale University, New Haven, Connecticut

(Received October 27, 1961)

The effect of the spin-orbit coupling on the long-range interatomic forces is computed. The representation is diagonal in the spin-orbit Hamiltonian of the two interacting atoms, and the electrostatic perturbation quantizes the total angular momentum  $\mathbf{J}$  along the internuclear axis. The theory is applied to the interaction of two atoms in the one-electron approximation. In particular, resonance interactions of normal and excited atoms, and the interaction energies between atoms in excited states are calculated. The use of a coupled representation is valid only as long as the electrostatic interaction is a true perturbation on the system. To investigate the transition from a representation in which spin effects are neglected to the one which includes the spin-orbit coupling correctly, a more general perturbation method is formulated.

## I. INTRODUCTION

IN all the previous calculations of the long-range interaction energies, the effect of the spin-orbit interaction has been neglected.<sup>1</sup> The use of eigenfunctions which do not include this coupling is certainly justifiable in those regions of space where the electrostatic interaction energy is much larger than the fine structure splitting. At large internuclear separations, however, the spin-orbit interaction in the two atoms will split the degenerate energy curves. In the case of the H-H interaction the degeneracy of the singlet and triplet curves is removed, and the number of energy curves is increased by a factor 4. All the results in Secs. III and IV are only valid as long as the condition  $V \ll H_{1, s_1} + H_{1, s_2}$  is satisfied. The region where  $V \simeq H_{1, s_1} + H_{1, s_2}$  is investigated in Sec. V. As in the previous two papers the theory will be applied to the interaction of two alkalis in the one-electron approximation. The methods, however, can be easily generalized to be applicable to any long-range force calculation.

## II. FIRST-ORDER ELECTROSTATIC MATRIX ELEMENTS

In the coupled representation, the normalized state function has the form

$$\Psi_{jm} = \sum_{m_l} C(ls j; m_l, m - m_l) \Psi_{l, m_l} \Psi_{s, m - m_l}. \quad (1)$$

This equation can be used to define the phases of the  $C$  coefficients. They are uniquely determined if we require that

$$(j' m' | j m) = \delta_{j', j} \delta_{m', m},$$

provided the  $\Psi_{lm_l}$  and  $\Psi_{sm_s}$  belong to orthonormal sets. The first-order matrix element is given by (II.1) if we redefine  $q$  to stand for  $j, m$ .

\* Part of a Dissertation presented to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

† Present address: Physics Department, The University of Chicago, Chicago, Illinois.

<sup>1</sup> See P. R. Fontana, Phys. Rev. **123**, 1865 (1961); **123**, 1871 (1961). All references to these papers will be denoted by I and II, respectively.

The factor  $(q' | Y_a^{\alpha*} | q)$  of (II.1) in the coupled representation could be evaluated in a straightforward way by using (II.2). The result, however, would involve a double summation, and this form is very inconvenient for numerical calculations. The summations can be eliminated by the following procedure: from (1) and (II.1) we have

$$(j' m' | Y_a^{\alpha*} | j m) = \sum_{m_l' m_l} C(l' s' j'; m_l', m' - m_l') \times C(ls j; m_l, m - m_l) (l' m_l' | Y_a^{\alpha*} | l m_l) \times \delta_{m' - m_l', m - m_l} \delta_{s', s}. \quad (2a)$$

The matrix element on the right-hand side of (2a) can be reduced by applying the Wigner-Eckart<sup>2,3</sup> theorem

$$(l' m_l' | Y_a^{\alpha*} | l m_l) = (-)^{\alpha} C(l a l'; m_l, -\alpha, m_l') \times (l' || Y_a || l). \quad (2b)$$

The  $C$  coefficient in (2b) contains the condition  $m_l - \alpha = m_l'$ , and one of the sums in (2a) can be eliminated. By using some symmetry relations of the  $C$  coefficients and introducing the Racah coefficient  $W$ , we can also eliminate the other sum.<sup>4-7</sup> The result is

$$(j' m' | Y_a^{\alpha*} | j m) = (-)^{s-l-i'+a+\alpha} [(2l'+1)(2j+1)]^{\frac{1}{2}} \times C(j a j'; m, -\alpha, m') W(l j l' j'; s a) (l' || Y_a || l). \quad (3)$$

Comparison of (II.2) with (2b) yields for the reduced matrix element

$$(l' || Y_a || l) = \left[ \frac{(2l+1)(2a+1)}{4\pi(2l'+1)} \right]^{\frac{1}{2}} C(l a l'; 000), \quad (4)$$

<sup>2</sup> E. P. Wigner, *Group Theory* (Academic Press, Inc., New York, 1959), p. 245.

<sup>3</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 85.

<sup>4</sup> G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943).

<sup>5</sup> L. C. Biedenharn, *Tables of the Racah Coefficients* (Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1952).

<sup>6</sup> U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press, Inc., New York, 1959), p. 84.

<sup>7</sup> Equation (3) differs from Eq. (6.24) in reference 3 by a factor of  $(-)^{j-j'}$ . This disagreement is not due to a different choice of the phases of the  $C$  and  $W$  coefficients. The transition from the coupled to the uncoupled representation cannot be made correctly if (6.24) of reference 3 is used.

and on combining (4) with (3), we have

$$(q' | Y_a^{\alpha*} | q) = (j'm' | Y_a^{\alpha*} | jm) = (-)^{s-l-i'+a+\alpha} \\ \times [(2j+1)(2l+1)(2a+1)/4\pi]^{\frac{1}{2}} \\ \times C(jaj'; m, -\alpha, m') C(lal'; 000) \\ \times W(lj'l'j'; sa). \quad (5)$$

As in (II.2) there is only one  $C$  coefficient which depends on the spatial orientation of the charge configurations. The transition from (5) to (II.2) can be made by setting  $s$  equal to zero. We then have  $j'=l', j=l$  and

$$(q' | Y_a^{\alpha*} | q) = (-)^{-l-l'+a+\alpha} \\ \times [(2l+1)(2l+1)(2a+1)/4\pi]^{\frac{1}{2}} \\ \times C(lal'; m, -\alpha, m') C(lal'; 000) \\ \times W(l'l'l'; 0a). \quad (6)$$

Now

$$W(l'l'l'; 0a) = (-)^{a-l-l'}/[(2l+1)(2l'+1)]^{\frac{1}{2}}, \quad (7)$$

and substitution of (7) into (6) yields

$$(q' | Y_a^{\alpha*} | q) = (-)^a [(2l+1)(2a+1)/4\pi(2l'+1)]^{\frac{1}{2}} \\ \times C(lal'; m, -\alpha, m') C(lal'; 000),$$

which is identical with (II.2).

The spin-orbit interaction removes some of the original degeneracy of the system, and thus the new secular determinant and molecular subdeterminants will be much smaller than those encountered previously. The factorization of the secular determinant has exactly the same characteristics as in the uncoupled representation. From (II.1) and (5) we see that the matrix elements are proportional to  $C(j_1aj_1'; m_1, -\alpha, m_1') \times C(j_2bj_2'; m_2, -\beta, m_2')$ . Combining the sum rules of the two  $C$  coefficients with the condition  $\alpha = -\beta$  from (I.6), we find that all matrix elements vanish unless  $m_1+m_2=m_1'+m_2'$ , and thus the total angular momentum  $\mathbf{J}=\mathbf{j}_1+\mathbf{j}_2$  is quantized along the internuclear axis with components  $\Omega=m_1+m_2$ . Similarly one can show that the eigenfunctions of (II.5) in the coupled representation have a definite symmetry under inversion through the center of the molecular system, and that the parity of the system does not change when the spin-orbit interaction is included. Thus all fine structure components have the same symmetry as the corresponding level before the inclusion of the spin.

In order to distinguish the molecular states in the coupled representation from those in paper II which have the orbital angular momentum quantized along  $\mathbf{R}$ , the numbers 0, 1, 2, ... are used to designate the total  $M_J$  of the molecular system.<sup>8</sup>

### III. RESONANCE INTERACTIONS OF NORMAL AND EXCITED ATOMS

Let us consider first the interaction of an alkali atom in the ground state with another one in the first-excited

state. The ground state consists of a  $1S_{\frac{1}{2}}$  level, whereas, the first-excited state is split into a  $2S_{\frac{1}{2}}$ ,  $2P_{\frac{1}{2}}$ , and a  $2P_{\frac{3}{2}}$  level. The fine structure splitting of the first-excited state divides the problem of calculating the electrostatic energy into three parts since we assume here that the levels are not being mixed by the electrostatic perturbation. The basic matrix elements can be obtained from paper II by substituting (II.A7) and (5) into (II.1). The first-order interaction energies between two dissimilar atoms are zero, and for the calculation of the resonance interaction energies the state functions of (II.5) are being used. All the results are exact solutions of the secular determinant. The  $1(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})$  and  $2(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  states are already in diagonal form; whereas, the remaining nonvanishing solutions are obtained from  $2 \times 2$  molecular subdeterminants.<sup>9</sup>

$$\text{a. } (1S_{\frac{1}{2}}, 2S_{\frac{1}{2}}): \quad 1(1S_{\frac{1}{2}}, 2S_{\frac{1}{2}}) = 0, \quad (8)$$

$$0(1S_{\frac{1}{2}}, 2S_{\frac{1}{2}}) = 0. \quad (9)$$

$$\text{b. } (1S_{\frac{1}{2}}, 2P_{\frac{1}{2}}): \quad 1_g(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}}) = -1_u(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}}) \\ = 2C/9Z_1^*Z_2^*R^3, \quad (10)$$

$$0_g(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_{\alpha} = 0_u(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_{\alpha} = 0, \quad (11)$$

$$0_g(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_{\beta} = -0_u(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_{\beta} \\ = -4C/9Z_1^*Z_2^*R^3. \quad (12)$$

$$\text{c. } (1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}): \quad 2_g(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -2_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) \\ = -C/3Z_1^*Z_2^*R^3, \quad (13)$$

$$1_g(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -1_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) \\ = (2-\sqrt{7})C/9Z_1^*Z_2^*R^3, \quad (14)$$

$$1_g(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -1_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) \\ = (2+\sqrt{7})C/9Z_1^*Z_2^*R^3, \quad (15)$$

$$0_g(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_{\alpha} = -0_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_{\alpha} \\ = -5C/9Z_1^*Z_2^*R^3, \quad (16)$$

$$0_g(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_{\beta} = -0_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_{\beta} \\ = 3C/9Z_1^*Z_2^*R^3. \quad (17)$$

The constant  $C$  in Eqs. (8-17) has the value 1.664787.  $Z_1^*$  is the effective nuclear charge of the  $1S_{\frac{1}{2}}$  state and  $Z_2^*$  the one of the respective level of the first-excited state. In those cases where the configuration interaction makes it impossible to assign a complete orbital configuration to the term symbol, the results are distinguished by subscripts  $\alpha, \beta$ . Here only the 0 states show such strong hybridization. The  $2_{g,u}(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  energy curves are identical with the two  $\Pi$  states of (II.8,9) in the uncoupled representation. In the generalized perturbation treatment in Sec. V it will be shown that this result is expected since the  $2_{g,u}$  states cannot combine with any other state of the complete

<sup>8</sup> R. S. Mulliken, Phys. Rev. **36**, 611 (1930).

<sup>9</sup> All the results are expressed in atomic units.

set which includes the  $(1S_{\frac{1}{2}}, 2S_{\frac{1}{2}})$ ,  $(1S_{\frac{1}{2}}, 2P_{\frac{1}{2}})$ , and  $(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  configuration.

In a similar way we have calculated the interaction energies between an alkali atom in the ground state and another one in the second excited state, both of which are in the coupled representation. The energy curves of the  $(1S_{\frac{1}{2}}, 3S_{\frac{1}{2}})$ ,  $(1S_{\frac{1}{2}}, 3P_{\frac{1}{2}})$ , and  $(1S_{\frac{1}{2}}, 3P_{\frac{3}{2}})$  states have exactly the same form as the ones in Eqs. (8-17), but with the constant  $C$  replaced by  $C'=0.2669678$ . The term symbols remain the same, and the only change in the orbital configuration is the replacement of  $n_2=2$  by  $n_2=3$ . The remaining interaction energies which have not been calculated previously are given below.

a.  $(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}})$ :

$$2_g(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}}) = -2_u(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}}) = -4D/25Z_1^{*2}Z_2^{*2}R^5, \quad (18)$$

$$1_g(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}}) = -1_u(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}}) = 16D/25Z_1^{*2}Z_2^{*2}R^5, \quad (19)$$

$$1_g(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{3}{2}}) = 1_u(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{3}{2}}) = 0, \quad (20)$$

$$0_g(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}})_\alpha = -0_u(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}})_\alpha = -24D/25Z_1^{*2}Z_2^{*2}R^5, \quad (21)$$

$$0_g(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}})_\beta = 0_u(1S_{\frac{1}{2}}, 3D_{\frac{3}{2}})_\beta = 0. \quad (22)$$

b.  $(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}})$ :

$$3_g(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = -3_u(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = D/5Z_1^{*2}Z_2^{*2}R^5, \quad (23)$$

$$2_g(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = -2_u(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = -11D/25Z_1^{*2}Z_2^{*2}R^5, \quad (24)$$

$$2_g(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{5}{2}}) = -2_u(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{5}{2}}) = -D/5Z_1^{*2}Z_2^{*2}R^5, \quad (25)$$

$$1_g(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = -1_u(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}}) = [19+3(89)^{\frac{1}{2}}]D/50Z_1^{*2}Z_2^{*2}R^5, \quad (26)$$

$$1_g(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{5}{2}}) = -1_u(1S_{\frac{1}{2}-\frac{1}{2}}, 3D_{\frac{5}{2}}) = [19-3(89)^{\frac{1}{2}}]D/50Z_1^{*2}Z_2^{*2}R^5, \quad (27)$$

$$0_g(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}})_\alpha = -0_u(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}})_\alpha = -26D/25Z_1^{*2}Z_2^{*2}R^5, \quad (28)$$

$$0_g(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}})_\beta = -0_u(1S_{\frac{1}{2}}, 3D_{\frac{5}{2}})_\beta = 2D/5Z_1^{*2}Z_2^{*2}R^5, \quad (29)$$

In the above equations, the constant  $D$  has the value 3.003388. The  $3_{g,u}$  states are identical with the  $\Delta$  states of (II.12) in the uncoupled representation. As in the previous calculation, no complete and unique orbital configuration can be assigned to the 0 states.

#### IV. INTERACTION ENERGIES BETWEEN ATOMS IN EXCITED STATES

In the calculation of the energy curves between two atoms both of which are in excited states, we have to

distinguish as in Sec. V of paper II between the resonance interactions of two identical atoms and the interactions of two dissimilar atoms. Because of the large number of energy curves in the coupled representation, we shall only calculate in detail the interaction energies between two alkali atoms in first-excited states. For the calculation of the energy curves between two dissimilar alkalis, we note that the  $(2S_{\frac{1}{2}}, 2S_{\frac{1}{2}})$ ,  $(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})$ , and  $(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  states do not give any non-vanishing first-order energies since the electrostatic perturbation cannot connect  $S$  states. The interaction energies obtained from the  $(2P_{\frac{1}{2}}, 2P_{\frac{1}{2}})$  and  $(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  configurations are likewise zero since the  $C$  coefficients in the matrix elements require that the multipole moment  $a$  in the interaction energy  $V$  assumes a value in the range  $j_1+j_1'\cdots|j_1-j_1'|$ , and that  $l_1+a+l_1'$  is even. But these conditions cannot be simultaneously satisfied by the  $2P_{\frac{1}{2}}$  state, and thus in the case of two interacting dissimilar alkali atoms in their first-excited states, only the  $(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}})$  configuration gives non-vanishing energies. All those results, however, can be obtained from the corresponding resonance calculation since in this case the exchange of states does not produce any new state functions of the system. The only difference in the two results is the meaning of the effective nuclear charges. In the first case, they refer to the  $2P_{\frac{3}{2}}$  states of different alkali atoms; whereas, in the second case, they are identical since the two  $2P_{\frac{3}{2}}$  states have the same energy.

In the following results, we have distinguished the two effective nuclear charges even in those cases where they are identical. In this way, the interaction energies between two dissimilar alkali atoms  $(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}})$  can also be obtained from the resonance calculations. The distinction between  $g$  and  $u$  states becomes then, of course, meaningless, and only the term symbol corresponding to the quantization of  $\mathbf{J}$  along the internuclear axis should be retained.

a.  $(2S_{\frac{1}{2}}, 2S_{\frac{1}{2}})$ :

$$1(2S_{\frac{1}{2}}, 2S_{\frac{1}{2}}) = 0, \quad (30)$$

$$0(2S_{\frac{1}{2}}, 2S_{\frac{1}{2}}) = 0. \quad (31)$$

b.  $(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})$ :

$$1_g(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}}) = -1_u(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}}) = 6/Z_1^{*2}Z_2^{*2}R^3, \quad (32)$$

$$0_g(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_\alpha = 0_u(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_\alpha = 0, \quad (33)$$

$$0_g(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_\beta = -0_u(2S_{\frac{1}{2}}, 2P_{\frac{1}{2}})_\beta = -12/Z_1^{*2}Z_2^{*2}R^3. \quad (34)$$

c.  $(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$ :

$$2_g(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -2_u(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -9/Z_1^{*2}Z_2^{*2}R^3, \quad (35)$$

$$1_g(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = -1_u(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}}) = (6+3\sqrt{7})/Z_1^{*2}Z_2^{*2}R^3, \quad (36)$$

$$1_g(2S_{\frac{1}{2}-\frac{1}{2}}, 2P_{\frac{3}{2}}) = -1_u(2S_{\frac{1}{2}-\frac{1}{2}}, 2P_{\frac{3}{2}}) = (6-3\sqrt{7})/Z_1^{*2}Z_2^{*2}R^3, \quad (37)$$

$$0_g(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\alpha = -0_u(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\alpha \\ = -15/Z_1^* Z_2^* R^3, \quad (38)$$

$$0_g(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\beta = -0_u(2S_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\beta = 9/Z_1^* Z_2^* R^3. \quad (39)$$

d.  $(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})$ :

All states have zero first-order interaction energies.

e.  $(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}})$ :

$$2_g(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}}) = -2_u(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}}) \\ = -144/Z_1^{*2} Z_2^{*2} R^5, \quad (40)$$

$$1_g(2P_{\frac{3}{2}-\frac{1}{2}}, 2P_{\frac{3}{2}}) = 1_u(2P_{\frac{3}{2}-\frac{1}{2}}, 2P_{\frac{3}{2}}) = 0, \quad (41)$$

$$1_g(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}}) = -1_u(2P_{\frac{3}{2}}, 2P_{\frac{3}{2}}) \\ = 576/Z_1^{*2} Z_2^{*2} R^5, \quad (42)$$

$$0_g(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\alpha = 0_u(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\alpha = 0, \quad (43)$$

$$0_g(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\beta = -0_u(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})_\beta \\ = -864/Z_1^{*2} Z_2^{*2} R^5, \quad (44)$$

f.  $(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}})$ :

$$3_g(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}}) = 216/Z_1^{*2} Z_2^{*2} R^5, \quad (45)$$

$$2_g(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}}) = -432/Z_1^{*2} Z_2^{*2} R^5, \quad (46)$$

$$2_u(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}}) = 0, \quad (47)$$

$$1_g(2P_{\frac{3}{2}-\frac{1}{2}}, 2P_{\frac{1}{2}}) = -144/Z_1^{*2} Z_2^{*2} R^5, \quad (48)$$

$$1_g(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}}) = 216/Z_1^{*2} Z_2^{*2} R^5, \quad (49)$$

$$1_u(2P_{\frac{3}{2}-\frac{1}{2}}, 2P_{\frac{1}{2}}) = -288/Z_1^{*2} Z_2^{*2} R^5, \quad (50)$$

$$0_g(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}})_\alpha = 504/Z_1^{*2} Z_2^{*2} R^5, \quad (51)$$

$$0_g(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}})_\beta = -72/Z_1^{*2} Z_2^{*2} R^5, \quad (52)$$

$$0_u(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}})_\alpha = 360/Z_1^{*2} Z_2^{*2} R^5, \quad (53)$$

$$0_u(2P_{\frac{3}{2}}, 2P_{\frac{1}{2}})_\beta = 72/Z_1^{*2} Z_2^{*2} R^5. \quad (54)$$

Again, the state with the highest  $M_J$  [ $3_g$  of Eq. (45)] is identical with the one in the uncoupled representation which has the highest  $M_L$  [ $\Delta_g$  of Eq. (II.17)].

## V. GENERALIZED PERTURBATION THEORY

We have already mentioned previously that the calculations in the coupled representation are only valid at large enough internuclear separations, where  $V \ll H_{1, s_1} + H_{1, s_2}$ . At smaller separations, one should not expect to obtain reliable results if the state functions which include the spin-orbit interaction are used; the energy curves in the uncoupled representation then appear to be closer to the correct values. If one plots the energy curves for the two representations corresponding to given states of the atoms, then one sees that the two sets of curves are quite different at large as well as at small internuclear separations. Clearly, a method is needed which joins the curves of the uncoupled representation at small separations with the ones which include spin-orbit interactions at large separations since at both ends the two different

methods should give good results. The conventional perturbation method, however, breaks down in the region where  $V \cong H_{1, s_1} + H_{1, s_2}$  since  $V$  is not a true perturbation in the coupled representation and the primitive set of simple product state functions which do not include the spin are poor approximations.

One way to bridge this gap is to apply a new perturbation  $H'$  which contains the electrostatic interaction between the two atoms as well as the spin-orbit interactions within the two atoms. Specifically let

$$H' = V + H_{1, s_1} + H_{1, s_2}. \quad (55)$$

The perturbation  $H'$  is then applied to the system which is described by simple product state functions including the spins, but which are not in a reduced representation.

If one now tries to solve the secular determinant for a given state of excitation of the two interacting atoms, one finds that  $H'$  has very undesirable symmetry properties. The electrostatic perturbation  $V$  factors the determinant according to the quantization of the total angular momentum along the internuclear axis. In addition, for resonance interactions, the symmetry of  $V$  makes it impossible to connect  $g$  and  $u$  states. On the other hand, the matrix elements of  $H_{1, s_1}$  and  $H_{1, s_2}$  contain the delta conditions  $l' = l$ ,  $s' = s$ ,  $m_l' + m_s' = m_l + m_s$ , and  $m_s' = m_s$ ,  $m_s \pm 1$  and thus factorize the secular determinant differently than does  $V$ .<sup>10</sup>

Let us now turn to the solution of the perturbation problem where  $H' = V + H_{1, s_1} + H_{1, s_2}$  is applied to the degenerate system in the uncoupled representation. There is little factorization of the secular determinant, and even for low-excited states the order of the determinant is much too large to be convenient for numerical calculations. One can, however, proceed further by making use of the fact 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. One possible reordering of the degenerate set is the transformation from the uncoupled to the coupled representation. From (1) we see that the state function  $\Psi_{jm}$  consists of a linear combination of the product functions  $\Psi_{lm_i} \Psi_{sm_s}$ . As long as we make sure that the new representation still extends over the complete degenerate set, the use of the  $\Psi_{jm}$  instead of the  $\Psi_{lm_i} \Psi_{sm_s}$  is a perfectly proper rearrangement of the original functions. Under this similarity transformation, the perturbation Hamiltonian  $H'$  now connects different states, and it is interesting to investigate the structure of the new secular determinant. The matrix elements of the electrostatic perturbation  $V$  in  $H'$  are zero unless the

<sup>10</sup> For the matrix elements of  $H_{1, s}$  in the uncoupled and coupled representation see for instance: E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 120, 257.

condition  $m_1 + m_2 = m_1' + m_2'$  is satisfied, and thus the secular determinant is made up of molecular sub-determinants which are designated by  $\Omega$ , the component of  $\mathbf{J}$  along the internuclear axis. In addition, this transformation reduces the representation of the spin-orbit Hamiltonians in  $H'$  completely, and  $H_{1_1, s_1}$  and  $H_{1_2, s_2}$  yield only diagonal elements. Thus  $H'$  has the same features as  $V$  and substantial factorization of the secular determinant is achieved.

To illustrate this method let us consider the interaction of two alkali atoms one of which is in the ground state and the other one in the first-excited state. The energy curves in the uncoupled representation can be obtained from Eqs. (II.8)–(II.10), and the ones in the coupled representation from Eqs. (8–17). In order to construct the secular determinant for  $H'$  in this case, we have to combine the  $(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  configuration with the  $(1S_{\frac{3}{2}}, 2P_{\frac{1}{2}})$  states. In this way, the complete degenerate set is being properly considered, and we have a correct perturbation problem also in the region where  $V \cong H_{1_1, s_1} + H_{1_2, s_2}$ . The secular determinant of the  $(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  states consists of one  $1_+$ , one  $0$ , and one  $1_-$  molecular subdeterminant, and from the  $(1S_{\frac{3}{2}}, 2P_{\frac{1}{2}})$  states, we obtain one  $2_+$ ,  $1_+$ ,  $0$ ,  $1_-$ , and  $2_-$  sub-determinant.<sup>11</sup> In the secular determinant of  $H'$ , we thus have only one  $2_+$  subdeterminant, and one can easily show that the resulting  $g$  and  $u$  states are already diagonal. This means that the corresponding energy curves consist of one part coming from the electrostatic perturbation and another one arising from the spin-orbit interactions. The second contribution can be subtracted out, and the remaining part is clearly identical with the result of the  $2_{g,u}$  states in the coupled representation. These energy curves, however, are also solutions of the generalized perturbation problem, and thus they are also valid at small internuclear separations where only the energy curves obtained from the uncoupled representation are expected to hold. This is the reason why the states with highest  $M_J$  in the coupled representation coincide with the one in the uncoupled representation which have the highest  $M_L$ .

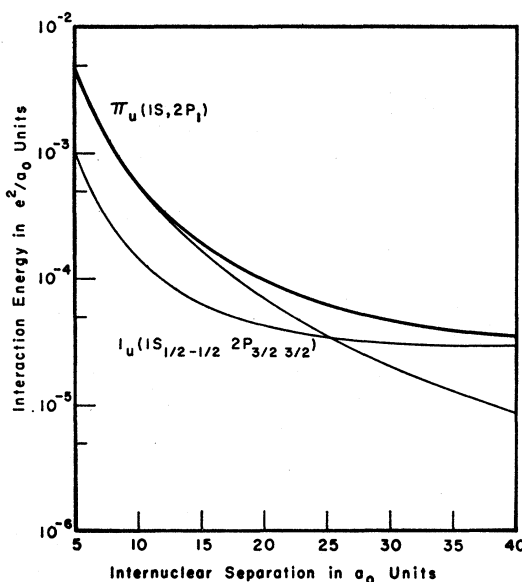


FIG. 1. Comparison of the energy curves in the uncoupled representation  $[\Pi_u(1S, 2P_1)]$  and coupled representation  $[1_u(1S_{\frac{1}{2}-1/2}, 2P_{\frac{3}{2}\frac{3}{2}})]$  with the corresponding curve of the generalized perturbation approach (heavy line). The  $1_u$  curve has the spin-orbit energy of the two atoms included.

In our case, the  $2_{g,u}$  states of (13) are identical with the  $\Pi$  states of (II.8,9).

The states obtained from the remaining subdeterminants, on the other hand, do not have this simple structure. For purposes of illustration, we have calculated the secular determinant in the generalized perturbation scheme whose solutions are identical with the  $1_u$  states of (10), (14), and (15) in the limit of very large internuclear separations.

Let us write the secular determinant as

$$|B - 1E| = 0, \quad (56)$$

where  $|B|$  has the form

$$\begin{aligned} & \frac{1}{\sqrt{2}} \begin{pmatrix} 0\frac{1}{2}\frac{1}{2}, 1\frac{1}{2}\frac{1}{2}; 1\frac{1}{2}\frac{1}{2}, 0\frac{1}{2}\frac{1}{2} \end{pmatrix} + \left[ \begin{array}{cc} \frac{-2C}{9Z_1^*Z_2^*R^3} + U & \frac{-\sqrt{6}C}{9Z_1^*Z_2^*R^3} \quad \frac{-2\sqrt{2}C}{9Z_1^*Z_2^*R^3} \\ \frac{-\sqrt{6}C}{9Z_1^*Z_2^*R^3} & V \quad \frac{\sqrt{3}C}{9Z_1^*Z_2^*R^3} \\ \frac{-2\sqrt{2}C}{9Z_1^*Z_2^*R^3} & \frac{\sqrt{3}C}{9Z_1^*Z_2^*R^3} \quad \frac{-4C}{9Z_1^*Z_2^*R^3} + W \end{array} \right] \end{aligned} \quad (57)$$

On the left of the determinant are written the quantum numbers of the state functions in the order  $l_1 j_1 m_1$ ;

<sup>11</sup> In accordance with the notation of paper II the subdeterminants are distinguished by the molecular designation  $\Omega = 0, 1_{\pm}, 2_{\pm}$ , etc., which corresponds to  $M_J = 0, \pm 1, \pm 2$ .

$l_2 j_2 m_2$ . The plus sign refers to  $\sigma = +1$  in Eq. (II.5). The value of the constant  $C$  is 1.664787, and the matrix elements of the spin-orbit interactions are denoted by  $U$ ,  $V$ , and  $W$ . If in (57) we set  $U = V = W = 0$ , then

we have the following three solutions of (56):

$$\begin{aligned} E_1 &= -2C/3Z_1^*Z_2^*R^3, & (^1\Sigma_u), \\ E_2 &= C/3Z_1^*Z_2^*R^3, & (^1\Pi_u), \\ E_3 &= -C/3Z_1^*Z_2^*R^3, & (^3\Pi_u). \end{aligned} \quad (58)$$

A comparison with the corresponding results in the uncoupled representation (II.8)–(II.10) and an analysis of the state functions show that these energy curves correspond to a  $^1\Sigma_u$ , a  $^1\Pi_u$ , and a  $^3\Pi_u$  state, respectively. In Fig. 1 we have plotted one of the exact solutions of (56) for the interaction of two H atoms (heavy line), together with the corresponding energy curves in the uncoupled and coupled representation. It is seen that the exact energy curve merges into the  $\Pi_u(1S, 2P_1)$   $\{^1\Pi_u, ^3\Pi_u\}$  curve of (II.9) at small internuclear separations, and it approaches asymptotically the energy

curve of the  $1_u(1S_{\frac{1}{2}}, 2P_{\frac{3}{2}})$  state at large  $R$ . The solution  $E_2(^1\Pi_u)$  corresponds to this curve at small internuclear separations.

It should be noted that the symmetry of the state functions under inversion through the center of the molecular system does not change when the spin-orbit interactions are included. In our specific case, all the energy curves obtained from the generalized perturbation treatment correspond to  $u$  states.

#### ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor Henry Margenau for suggesting this problem and also for the many helpful discussions during the course of this work. Financial support for this research from the Office of Naval Research is gratefully acknowledged.

## Structure and Photodetachment Spectrum of the Atomic Carbon Negative Ion\*

MICHAEL L. SEMAN AND LEWIS M. BRANSCOMB  
National Bureau of Standards, Washington, D. C.

(Received October 17, 1961)

The continuous absorption (photodetachment) spectrum of a beam of atomic carbon negative ions from a hot cathode arc was measured in the spectral region 0.4 to 2.6  $\mu$ . Between 0.4 and 0.8  $\mu$  the  $C^-$  photodetachment cross section was measured relative to that for  $O^-$  and was found to be almost independent of wavelength, consistent with the assignment of  $^4S$  to the  $C^-$  ground state. In this region the  $C^-$  cross section is approximately twice that for  $O^-$ . The variation of the absorption near one micron is consistent with the expected threshold behavior and yields a value for the ground-state binding energy (carbon electron affinity) of  $1.25 \pm 0.03$  ev. Weak absorption in the region from 1 to 2.6  $\mu$  is felt to demonstrate the stability of a metastable negative-ion state, probably  $C^- 1s^2 2s^2 2p^3 ^2D$ . No such absorption is observed at wavelengths longer than the ground-state threshold in  $O^-$ , in which metastable states are not expected.

### I. INTRODUCTION

THIS measurement of the continuous absorption coefficient (or photodetachment cross section) for the atomic carbon negative ion,  $C^-$ , completes a series of studies of the atomic negative ions of interest as sources of opacity in stellar atmospheres. Data for  $H^-$  and  $O^-$  have been reported elsewhere.<sup>1,2</sup> A general discussion of the possible contribution of negative ions other than  $H^-$  to stellar opacities suggests that ions such as  $O^-$  and  $C^-$  are likely to be important in cooler stars of unusual composition.<sup>3</sup>

Other than the present results, no measurements and no significant calculations of the photodetachment cross section for  $C^-$  have been published. The experi-

mental evidence regarding the binding energy of the ground state consists of an estimate from the rate of sublimation of  $C^-$  ions from a carbon filament<sup>4</sup> and two measurements (unpublished) of the difference between the electron affinities of C and O obtained by electron impact in CO.<sup>5,6</sup> These values, which are summarized in Table III, indicate a threshold for photodetachment from the  $C^-$  ground state in the region of 1  $\mu$ , corresponding to a binding energy in the vicinity of 1.2 ev.

With regard to the existence of states of  $C^-$  other than the ground state there is even less information. Theoretical and semiempirical evidence<sup>7,8</sup> suggests that

\* R. E. Honig, J. Chem. Phys. **22**, 126 (1954).

<sup>5</sup> C. R. Lagergren, Ph.D. thesis, University of Minnesota, 1955 (unpublished).

<sup>6</sup> M. A. Fineman and A. Petrocelli (private communication) and Bull. Am. Phys. Soc. **3**, 258 (1958).

<sup>7</sup> H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1950), 2nd ed.

<sup>8</sup> D. R. Bates, Proc. Roy. Irish Acad. **A51** (1947) and D. R. Bates and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A68**, 540 (1955).

\* Supported in part by the Office of Naval Research.

<sup>1</sup> S. J. Smith and D. S. Burch, Phys. Rev. **116**, 1125 (1959).

<sup>2</sup> S. J. Smith, *Proceedings Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), p. IC219.

<sup>3</sup> L. M. Branscomb and B. E. F. Pagel, Monthly Notices Roy. Astron. Soc. **118**, 258 (1958).