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# Application of the Group $R_4$ to Energy-Level Separations and the Evaluation of Correlation Energy in Atoms

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The group $R_4$ is applied to the study of energy-level separations and correlation energies in the ground-state configurations of first-row atoms. The separation between two nearly degenerate levels, e.g., $2s^2\ {}^1S$ and $2p^2\ {}^1S$, considering the $\sum_{i>j} 1/r_{ij}$ part of the Hamiltonian only, can then be determined by means of group theory, eliminating the need of solving the secular equation arising from the usual configuration-interaction procedure. Extending this work to the one-electron part of the Hamiltonian enables us to estimate the actual splittings and the $\epsilon(2s^2)$ nondynamical (near degeneracy) correlation energy for the first-row atoms. The $Z$ and $N$ dependence of this type of correlation is seen to be closely related to the group theoretical treatment. Finally this method is extended to a treatment of the nondynamical correlation in second-row atoms.

In the usual approaches to the problem of the effects of electron correlation, configuration-interaction methods are used to determine the interaction among closely lying configurations of the same $R_3$ symmetry. In a previous paper[1] we used the group $R_4$ to classify the energy levels of atoms containing more electrons than hydrogen. Here we treat $R_4$ as a starting point for our study of the energy levels and treat the many-electron effects as a perturbation of the group symmetry. Using $R_4$ we determine energy-level separations and "nondynamical"-type (near degeneracy) correlation effects in first-row atoms. In addition the dependence of this correlation energy on $Z$, the nuclear charge, and on $N$, the number of electrons, is discussed. Finally we extend the work to a preliminary study of second-row atoms for which there are very few configuration-interaction calculations.

We begin by discussing correlation energy from the point of view of the "many-electron theory" of Sinanoğlu,[2] emphasizing the nondynamical type which will be considered in this work. After briefly outlining the conventional method of calculation, the group-theoretical approach is described for first-row atoms. The $Z$ and $N$ dependence of the nondynamical correlation is elucidated and finally the extension to second-row atoms is carried out.

## I. THE NATURE OF ELECTRON CORRELATION

The correlation energy of a system is defined as the difference between the exact nonrelativistic energy of the system and the Hartree-Fock energy. If $\phi_0$, $E_{\text{HF}}$ are the Hartree-Fock wave function and energy respectively, and $\chi$, $E_{\text{cor}}$ are the correlation wave function and energy, then the exact wave function and energy can be written as

$$\psi=\phi_0+\chi,\quad E=E_{\text{HF}}+E_{\text{cor}}, \tag{1}$$

$$\text{where}\quad \langle\phi_0|\phi_0\rangle=1,\quad \langle\chi|\phi_0\rangle=0. \tag{2}$$

Sinanoğlu[2] has shown that the correlation energy for atoms may be apportioned among the various pairs of electrons in the system, and that in general, correlation effects arising from the simultaneous interactions involving more than two electrons can be neglected. Thus to a good approximation

$$\chi=\sum_{i>j=1}^{N}\frac{\mathcal{A}}{\sqrt{2}}\left\{(12\cdots N)\frac{\hat{u}_{ij}}{ij}\right\},$$
$$E_{\text{cor}}=\sum_{i>j}\epsilon_{ij} \tag{3}$$

where $\hat{u}_{ij}$ are pair-correlation wave functions and $\epsilon_{ij}$ are decoupled pair-correlation energies. Furthermore, the correlation energy for each pair of electrons may be divided into a dynamical part that is essentially independent of the atom, and a nondynamical part which can not be transferred from atom to atom. This nondynamical correlation arises from the effects of the interaction of the ground configuration with a small number of nearly degenerate configurations. Thus the correlation energy of the two $2s$ electrons in Be, $\epsilon(2s^2)$, arises primarily from the interaction of the two lowest singlet $S$ configurations, namely, $1s^22s^2\,{}^1S$ and $1s^22p^2\,{}^1S$.

Since dynamical correlation is transferable, it is possible to treat it semi-empirically. That is, once a value for the dynamical energy of a particular pair is obtained for one atom, this value can be used for the same pair in any other atom or ion. The nondynamical correlation clearly presents more of a problem, since it must be calculated for each atom. The nature of the nontransferability, that is, its dependence on $Z$ (nuclear charge) and $N$ (number of electrons) has been discussed previously; the $Z$ dependence by Layzer,[3] and Linderberg and Shull,[4] the $N$ dependence by McKoy and Sinanoğlu.[5] Here we shall relate this $Z$ and $N$ dependence to the properties of the group $R_4$. To a good approximation, the nondynamical correlation for two $2s$ electrons is a linear function of these $Z$ and $N$ parameters. We shall attempt the calculation of $\epsilon(2s^2)$ using $R_4$ group theory. This procedure gives a more mathematical and physical interpretation to the nondynamical correlation energy effect.

The usual method for calculating nondynamical correlation and the related energy-level separations makes use of configuration interaction.[6] Let us assume, as is the case for first-row atoms, that there is just one excited state which has the same symmetry as the ground state and is fairly close in energy to this ground state. Then if $E_1$ and $E_2$ are the Hartree-Fock energies of the ground and of the excited configurations, respectively, $\lambda_{\min} - E$ is the nondynamical correlation energy, and $\lambda_{\max} - \lambda_{\min}$ is the splitting where $\lambda_{\min}$, $\lambda_{\max}$ are the smaller and larger roots of the secular equation

$$\begin{vmatrix} E_1 - \lambda & K \\ K & E_2 - \lambda \end{vmatrix} = 0 \; , \tag{4}$$

and $K$ is the interaction matrix element between the two configurations.

## II. THE GROUP-THEORETICAL APPROACH

We will now discuss a more group-theoretical method for determining splittings and nondynamical correlation. We have seen in paper I how the four-dimensional rotation group $R_4$ can be applied to atoms containing more than one electron. The transformation properties under $R_4$ of various configurations of first-row atoms were derived and Coulomb and exchange integrals calculated. In the process of evaluating the integrals, the two-particle Coulomb operator $G = \sum_{i>j} 1/r_{ij}$ was expressed in terms of tensors transforming according to irreducible representations of $R_4$. It is this two-particle Coulomb operator which is responsible for the interaction between the configurations and thus for the nondynamical correlation. This is true since only the two-electron operator $G$ of the Hamiltonian has nonzero matrix elements between two configurations differing by two orbitals, e.g., $1s^2 2s^2$ and $1s^2 2p^2\,{}^1S$ of Be. Therefore we determine the splitting due to this part of the Hamiltonian alone. The effect of the remainder of the Hamiltonian, the part that gives rise to energy differences due to the inequality of $I_{2s}$ and $I_{2p}$, is introduced as a correction. $I_{2s}$ and are the Slater $I$ parameters,[7] one-electron integrals of the form

$$\int \phi^*(1)[-\hbar^2/2m + U]\,\phi(1)\,d\tau_1 \; .$$

If the atom were exactly $R_4$ symmetric, then $I_{2s} = I_{2p}$, and the splitting would arise entirely from the two-electron part of the Hamiltonian and no correction would be necessary.

### A. Splitting Due to the Two-electron Part of the Hamiltonian

We consider Be as an example for the calculation of the splitting caused by the interaction of the $1s^2 2s^2\,{}^1S$ and $1s^2 2p^2\,{}^1S$ configurations and of the nondynamical correlation energy. Using the familiar Slater $I$, $F$, and $G$ parameters,[7,8] the Hartree-Fock levels for the ground and excited configurations can be expressed by

$$E_{1s^2 2s^2}^{\mathrm{HF}} = 2I_{1s} + 2I_{2s} + F_0(1s,1s) + 4F_0(1s,2s) - 2G_0(1s,2s) + F_0(2s,2s), \tag{5}$$

$$E_{1s^2 2p^2\,{}^1S}^{\mathrm{HF}} = 2I_{1s} + 2I_{2p} + F_0(1s,1s) + 4F_0(1s,2p) - 2G_1(1s,2p) + F_0(2p,2p) + 10F_2(2p,2p), \tag{6}$$

or

$$E_{1s^2 2s^2}^{\mathrm{HF}} = 2I_{1s} + 2\eta_{2s} + F_0(2s,2s) \; , \tag{7}$$

$$E_{1s^2 2p^2\,{}^1S}^{\mathrm{HF}} = 2I_{1s} + 2\eta_{2p} + F_0(2p,2p) + 10F_2(2p,2p) \; , \tag{8}$$

where

$$\eta_{2s} = I_{2s} + 2F_0(1s,2s) - G_0(1s,2s) \; , \tag{9}$$

$$\eta_{2p} = I_{2p} + 2F_0(1s,2p) - G_1(1s,2p) \; . \tag{10}$$

Thus $\eta_{2s}$, $\eta_{2p}$ are the Hartree-Fock orbital energies of a hypothetical Be$^+$ ion as it exists in the Be atom, using the Hartree-Fock orbitals of Be. Since we are concerned with energy differences only, the energy scale is irrelevant and we can subtract the common term $2I_{1s}$ from each of (5) and (6). We may regard this term as a "vacuum" energy. Let us now make the approximation that our system possesses $R_4$ symmetry. We note that the $1s^2$ part we have dropped does itself transform according to the identity representation of $R_4$. We now consider an average $\eta$ instead of $\eta_{2s}$ and $\eta_{2p}$ since, if we in fact did have $R_4$ symmetry, the orbital energies for a $2s$ and $2p$ electron would be the same. The term is now common to both (7) and (8), and so it too may be subtracted from each expression. These $\eta$ terms may be regarded as "self-energy" terms since they represent the interaction of the $2s$ or the $2p$ orbital with itself and the vacuum. We are now left with the two-electron interaction terms,

$$E_{1s^2 2s^2\,{}^1S}^{J} = F_0(2s,2s), \tag{11}$$

$$E_{1s^2 2p^2\,{}^1S}^{J} = F_0(2p,2p) + 10F_2(2p,2p) \; , \tag{12}$$

and can apply the $R_4$ methods discussed previously.

The various states of the Be atom have been classified with respect to irreducible representations of $R_4$. Following the discussion in the preceding paragraph, we consider here electrons with principal quantum number 2 only. This does not affect the symmetry classification, since the $n=1$ shell is completely filled and thus transforms according to the identity representation of $R_4$. Since $R_4$ is a larger group than $R_3$, the ordinary three-dimensional rotation group, and includes $R_3$ as a subgroup, $R_4$ relates configurations having the same $R_3$ symmetry. For example, the two ${}^1S$ states of Be we are treating can be combined to transform as the (00) and (20) representations of $R_4$. Thus

$$(00)S = [\tfrac{1}{2}(2s^2) - (\sqrt{3}/2)(2p^2)]\,S\,,$$

$$(20)S = [(\sqrt{3}/2)(2s^2) + \tfrac{1}{2}(2p^2)]\,S\,, \tag{13}$$

It has been predicted by Sinanoğlu that combinations of $2s^2$ and $2p^2$ transforming according to irreducible representations of $R_4$ would come close to the combinations obtained by means of two-by-two configuration interaction. The mixing of these two states in Be is similar to the mixing of the ground-configuration wave function of metastable He, $2s^2\,{}^1S$, with the excited configuration $2p^2\,{}^1S$, provided of course that we use the proper orbitals for metastable He. Wulfman[9] has pointed out the extremely good agreement between the coefficients obtained by classification according to $R_4$ and the coefficients obtained from a configuration calculation using a hydrogenic basis limited to orbitals with principal quantum number 2 as calculated by Lipsky and Russek.[10] The ratios $2s^2$: $2p^2$ in the $R_4$ states are 0.587 and 1.732, while the Lipsky and Russek ratios are 0.56 and 1.726.

If we now evaluate the $a_1(000)$ part of the Coulomb interaction[1] for each of the states described in Eqs. 13, we see that the two $R_4$ states are nearly degenerate with respect to an $R_4$-symmetric Hamiltonian. The entire Coulomb operator $G$ splits this near degeneracy. This operator does not commute with $R_4$; it is not an $R_4$-symmetric operator. Its transformation properties can be found and were determined in Sec. III of the preceding paper. We saw that the Coulomb operator giving nonzero matrix elements between configurations, all of whose electrons have principal quantum number 2, was a linear combination of tensors transforming as the (000), (200), and (400) irreducible representations of $R_4$. The diagonal matrix elements of this operator for either state of Be, i.e. either of the (00) or (20) irreducible representations, may be calculated using the Wigner-Eckart Theorem. Since both the $R_4$ Clebsch-Gordan coefficients and the reduced matrix elements for $R_4$ are known, the calculation of the diagonal matrix elements is easily effected. If the description of the states using $R_4$ remains satisfactory after the introduction of the $G$ potential, then the difference in the diagonal matrix elements will give a good approximation to the actual splitting.

To continue with our example of the splitting of the two lowest ${}^1S$ states of Be, we evaluate the diagonal matrix elements $\langle(00)|G|(00)\rangle$ and $\langle(200)|G|(200)\rangle$. The level separation as given by $R_4$ is simply the difference between these two terms. Making use of the Clebsch-Gordan coefficients for $R_4$ and the numerical values for the parameters in the $G$ potential previously calculated, we can now evaluate the splitting.

We can compare this value of the splitting with the actual two-configuration interaction for the $E^J$ part of the problem only. Thus we solve the equation

$$\begin{vmatrix} F^0(2s,2s)-\lambda & (1/\sqrt{3}\,)G^1(2s,2p) \\ (1/\sqrt{3}\,)G^1(2s,2p) & F^0(2p,2p)+\frac{2}{5}F^2(2p,2p)-\lambda \end{vmatrix} = 0\,, \tag{14}$$

The results of these calculations, using Hartree-Fock orbitals, are given in Table I. The values calculated by means of $R_4$ and those obtained by solving the secular equation using hydrogen orbitals for each method do not agree with each other at all. Hartree-Fock orbitals give this better agreement because they are more diffuse than hydrogenic ones. Consequently the $2s^2$ and $2p^2$ levels are more nearly degenerate and thus fit more closely the model of the splitting of degenerate levels. Again we emphasize that this discussion deals with the $E^J$ part only without the "self-energy" correction. This correction is discussed in the next section.

In this treatment we are ignoring the off-diagonal matrix element $\langle(00)|\sum 1/r_{ij}|(20)\rangle$. If this term were included and the usual degenerate perturbation theory applied, we would get exactly the same result as we do in the ordinary configuration interaction method, i.e., the result of Eq. (14). It makes no difference which linear combination of configurations we take as the unperturbed functions. Diagonalizing and solving the secular equation will always yield the same eigenvalues and eigenfunctions. The importance of the $R_4$ approach lies in the fact that group theory enables us to obtain a very good approximation to the exact calculation. In other words, after making the transformation from the configuration $2s^2\,{}^1S$, $2p^2\,{}^1S$ to those linear combinations which transform according to irreducible representations of $R_4$, the off-diagonal matrix elements become small in comparison with the difference between the diagonal elements. We have essentially diagonalized the Hamiltonian matrix group theoretically, and are justified in our assumption that the $R_4$ classification scheme

TABLE I. Splittings arising from the two-electron operator part of the Hamiltonian (in a.u.).

| | Calculated using $R_4$ | Calculated using configuration-interaction Hartree-Fock orbitals |
|---|---|---|
| Be ${}^1S$ | 0.272 | 0.280 |
| B ${}^2P$ | 0.246 | 0.257 |
| C ${}^3P$ | 0.229 | 0.231 |

remains good even after the introduction of the Coulomb interaction.

### B. The Self-Energy Correction

We must now correct for the fact that $\eta_{2s} \neq \eta_{2p}$ and the fact that the two Hartree-Fock configurations do interact. If there were no interaction between the Hartree-Fock levels, the splitting for Be would be simply

$$[2(\eta_{2p} - \eta_{2s})] + [F_0(2p, 2p) + 10F_2(2p, 2p) - F_0(2s, 2s)] \tag{15}$$

In the previous section we saw the effect that the interaction has on the second term of Eq. (15). We must now make a correction for the effect of the interaction on the first term and determine the correction to the self-energy.

We will obtain an expression for this correction by adding an operator to the Hamiltonian with the following properties. The operator is expressed in terms of irreducible tensors transforming according to $R_4$. The coefficients of these tensors are the orbital energies $\eta_{nl}$ defined previously, where $n$ is the principal quantum number and $l$ is the angular momentum quantum number. The orbital wave functions are eigenfunctions of this operator with eigenvalues equal to the appropriate orbital energies $\eta_{nl}$. It will be seen that there is a natural way of determining this operator.

Let us first consider a special case of this operator in which $\eta_{nl}$ is set equal to $\eta_{nl'}$. We denote this operator by $C$. $C$ is a sum of one-electron operators $c_i$, where $i$ is the number of electrons in the system under consideration. For the sake of simplicity we will omit the subscript $i$ when it is not important to specify a particular $c_i$. By setting $\eta_{nl} = \eta_{nl'}$, i.e. equating orbital energies of electrons of the same principal quantum number $n$, we are saying that $R_4$ symmetry is retained. The operator $c$ has the same value when applied to all orbitals of the same $n$, or in other words it has the same value when applied to any row of a particular representation of $R_4$. If the value of an operator is entirely specified by the representation of the state on which it acts, it must be completely symmetrical with respect to $R_4$ and must transform like the identity representation. We can write this operator in the form of a second-degree homogeneous function of the partners of the basic representation, i.e., the (10) representation of $R_4$. We therefore have

$$c = \eta[\alpha(1000)(1000) + \beta(1010)(1010) + \gamma(1011)(101-1) + \delta(101-1)(1011)]. \tag{16}$$

Because $c$ is a completely symmetrical one-electron operator, we can easily find the values of the constants $\alpha$, $\beta$, $\gamma$, and $\delta$ using the reduction formula for the $R_4$ spherical harmonics given by Shibuya and Wulfman.[11] We see that

$$\begin{aligned} \alpha &= \mathcal{C}[(0000)(0000)\,|\,(1000)] = 1, \\ \beta &= \mathcal{C}[(1010)(1010)\,|\,(1000)] = 1, \\ \gamma &= \mathcal{C}[(1011)(101-1)\,|\,(1000)] = -1, \\ \delta &= \mathcal{C}[(101-1)(1011)\,|\,(1000)] = -1, \end{aligned} \tag{17}$$

where the $\mathcal{C}$ are the one-electron reduction coefficients. Using these values of $\alpha$, $\beta$, $\gamma$, and $\delta$ we have

$$c = \tfrac{1}{4}\eta[(1000)(1000) + (1010)(1010) - (1011)(101-1) - (101-1)(1011)]. \tag{18}$$

The factor of $\frac{1}{4}$ is inserted so that $c$ will have the value $\eta$ when evaluated on any state of principal quantum number 2. We now modify the operator to take into account the fact that $\eta_{2s} \neq \eta_{2p}$. The operator must give $\eta_{2s}$ when applied to a $2s$ orbital and $\eta_{2p}$ when applied to a $2p$ orbital. This modification can be accomplished by setting

$$c' = e_1 + e_2 + e_3 + e_4,$$

such that

$$e_1(2s) = \eta_{2s}(2s), \quad e_2(2p_0) = \eta_{2p}(2p_0),$$
$$e_3(2p_+) = \eta_{2p}(2p_+), \quad e_4(2p_-) = \eta_{2p}(2p_-),$$

and all other combinations, e.g. $e_1(2p_+)$, give zero. This decomposition is easily effected and it is found that

$$\begin{aligned} e_1 &= \tfrac{1}{4}\eta_{2s}[\tfrac{5}{2}(1000)(1000) - \tfrac{1}{2}(1010)(1010) + \tfrac{1}{2}(1011)(101-1) + \tfrac{1}{2}(101-1)(1011)], \\ e_2 &= \tfrac{1}{4}\eta_{2p}[-\tfrac{1}{2}(1000)(1000) + \tfrac{5}{2}(1010)(1010) + \tfrac{1}{2}(1011)(101-1) + \tfrac{1}{2}(101-1)(1011)], \\ e_3 &= \tfrac{1}{4}\eta_{2p}[-\tfrac{1}{2}(1000)(1000) - \tfrac{1}{2}(1010)(1010) - \tfrac{5}{2}(1011)(101-1) + \tfrac{1}{2}(101-1)(1011)], \\ e_4 &= \tfrac{1}{4}\eta_{2p}[-\tfrac{1}{2}(1000)(1000) - \tfrac{1}{2}(1010)(1010) + \tfrac{1}{2}(1011)(101-1) - \tfrac{5}{2}(101-1)(1011)]. \end{aligned} \tag{19}$$

We now allow $C = \sum c_i'$ to act on the states transforming according to the irreducible representations of $R_4$ that we found previously. To find the correction to the splitting we must calculate

$$C'(200) - C'(000). \tag{20}$$

This result could of course have been obtained by simply noting the coefficients of the linear combination of the $2s^2$ and $2p^2$ configurations and using the Slater-Condon rules for one-electron operators. However the method used here shows more clearly the group-theoretical basis for the correction.

Thus the self-energy part of the energy difference for Be can be expressed as

$$2(\eta_{2s} - \eta_{2p}) + C'[(200) - (000)] \tag{21}$$

For boron there is an analogous expression. For carbon however it is necessary to make an additional correction. The type of operator used above gives information about the relative number of $p$ electrons with respect to $s$ electrons. It yields no information about the coupling of the $p$ electrons. For carbon the operator $C$ gives the same correction for each of the three states transforming according to irreducible representations of $R_4$ describing the configurations $2s^22p^2$ and $2p^4$. We have

$$(200)=[(1/\sqrt{2})(2s^22p^2)-(1/\sqrt{2})(2p^4)]\ {}^1S,$$
$$(201)=[(1/\sqrt{2})(2s^22p^2)-(1/\sqrt{2})(2p^4)]\ {}^3P,$$
$$(202)=[(1/\sqrt{2})(2s^22p^2)-(1/\sqrt{2})(2p^4)]\ {}^1D\,.$$

These three states (200), (201), and (202) are the linear combinations of ${}^1S$, ${}^3P$, and ${}^1D$ configurations, respectively. The correction is the same in each case because corresponding coefficients of the configurations are the same for each state. For example the coefficient of the $(2p^4)$ configuration is $-1/\sqrt{2}$ for each of the three states (200), (201), and (202). The same relations hold true for the other $R_4$ states for these configurations (000), (111), and (222), so that the correction to the energy difference of the two $R_4$ states for each of the ${}^1S$, ${}^3P$, ${}^1D$ symmetries is the same. For beryllium (with no $p$ electrons in the ground state) and for boron (one $p$ electron) there is no ambiguity, but for carbon the nature of the coupling must be introduced explicitly. The Young diagrams for the space and spin parts of the $p^2$ configuration are helpful in this context. The space-spin diagrams for the ${}^1S$, ${}^1D$, and ${}^3P$ states are given in Fig. 1. Only for the ${}^3P$ and the ${}^1D$ case is it possible to have two of the same entries in one diagram. That is, the orbital part of ${}^1D$ and the spin part of ${}^3P$ can be represented by the diagrams given in Fig. 2. Therefore we expect the correction to the one-electron part of the interaction to be the same for the ${}^1D$ and ${}^3P$ terms but different from the ${}^1S$ term. In fact, the correction must again be proportional to the difference in orbital energies with a coefficient equal to the maximum number of pairs of identical entries possible in either one of the space or spin Young diagrams. This type of correction gives rise to a nonvanishing term for carbon only.

## III. ENERGY LEVEL SEPARATIONS AND NONDYNAMICAL CORRELATION

The total splitting between the two lowest singlet $S$ levels of our model Be atom may now be obtained by simply summing the various contributions already determined in the previous two subsections. The results for Be, as well as for B and C, together with a comparison with the actual calculation using two-by-two configuration interaction [see Eq. (14)] are shown in Table II. We see that the $R_4$ calculated values for the splittings are in agreement with those calculated by configuration interaction.

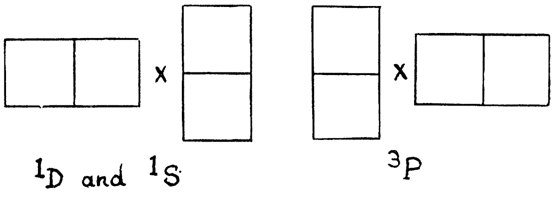

FIG. 1. Young diagrams for the ${}^1D$, ${}^1S$, and ${}^1P$ states.

FIG. 2. Young diagrams for (a) the orbital part of ${}^1D$, and (b) the spin part of ${}^3P$.

The $\epsilon(2s^2)$ nondynamical correlation energy may now be obtained very simply from the value of the splitting. Thus

$$\epsilon(2s^2)=\tfrac{1}{2}(E_{\mathrm{I}}-E_{\mathrm{II}}), \tag{22}$$

where $E_{\mathrm{II}}$ is the difference in energy between the $R_4$ symmetrical states, e.g. (20) and (00) in Be, and $E_{\mathrm{I}}$ is the difference in energy between the unmixed configurations, e.g. $1s^22s^2\,{}^1S$ and $1s^22p^2\,{}^1S$ in Be. Table III gives this $\epsilon(2s^2)$ nondynamical correlation calculated by the use of $R_4$ for the ground states of the first-row atoms Be through Ne, and gives the corresponding values for the actual atoms as given by McKoy and Sinanoğlu.[5]

We now consider other aspects of the nondynamical correlation. How does $\epsilon(2s^2)$ vary as $Z$ (nuclear charge) is increased while $N$ (number of electrons) is kept constant? Linderberg and Shull[4] showed that if hydrogen functions are used $\epsilon(2s^2)$ can be expected to be linear in $Z$. They expanded the expressions for the energy of the single ground-state configuration and of the best linear combination of the two lowest configurations of the same symmetry for the Be isoelectronic sequence in powers of $Z$.

$$\begin{aligned} E_{1s^22s^2}^{\mathrm{HF}} &= -1.25Z^2+1.559Z-\cdots, \\ E_{\text{two config.}} &= -1.25Z^2+1.571Z-\cdots. \end{aligned} \tag{23}$$

The difference in energy between these two expressions is the nondynamical $\epsilon(2s^2)$. The terms

TABLE II. Splittings arising from the entire Hamiltonian (in a.u.).

| | Calculated using $R_4$ | Calculated using configuration interaction |
|---|---|---|
| Be ${}^1S$ | 0.454 | 0.448 |
| B ${}^2P$ | 0.581 | 0.577 |
| C ${}^3P$ | 0.784 | 0.780 |

TABLE III. $\epsilon(2s^2)$ Nondynamical correlation energy for first-row atoms (in a.u.).

| | Calculated using $R_4$ | Calculated using configuration interaction | Calculated by McKoy and Sinanoğlu[5] |
|---|---|---|---|
| Be $^1S$ | $-0.045$ | $-0.042$ | $-0.0416$ |
| B $^2P$ | $-0.032$ | $-0.030$ | $-0.0298$ |
| C $^3P$ | $-0.0185$ | $-0.017$ | $-0.0168$ |
| N $^4S$ | 0 | 0 | 0 |
| O $^3P$ | 0 | 0 | 0 |
| F $^2P$ | 0 | 0 | 0 |
| Ne $^1S$ | 0 | 0 | 0.0005 |

quadratic in $Z$ cancel because $I_{2s}=I_{2p}$ and the only other important terms are linear in $Z$. Let us now look at the $Z$ dependence using the $R_4$ picture.

The coefficients of the configurations comprising an $R_4$ symmetric state are independent of $Z$. Thus for example in dealing with a system with two electrons of principal quantum number two, Be, B$^+$, C$^{++}$, $\cdots$ ,

$$(20)S=(\sqrt{3}/2)(1s^2 2s^2\,{}^1S)-\tfrac{1}{2}(1s^2 2p^2\,{}^1S)\,. \tag{24}$$

The $\sqrt{3}/2$ and $\frac{1}{2}$ are constants independent of $Z$; $2s^2$, $2p^2$ are the properly chosen Hartree-Fock orbitals for the particular member of the isoelectronic sequence under discussion. Since the correction to the self-energy term is also based on the $R_4$ symmetric functions, its form is also invariant among the members of an isoelectronic sequence. If we write the correlation energy for, say the Be isoelectronic sequence, using equations (20) and (22) we find

$$\begin{aligned}\epsilon(2s^2)=\tfrac{1}{2}\{&C'[(20)-(00)]+\tau\\ &-[F^0(2s,2s)-F^0(2p,2p)-\tfrac{2}{5}F^2(2p,2p)]\}\ ,\end{aligned} \tag{25}$$

where $\tau$ is the two-electron contribution to the splitting calculated in Sec. II. Equation (25) is composed of Coulomb and exchange integrals which appear in the second and third terms of (25) together with one-electron orbital energies of the form $k(\eta_{2p}-\eta_{2s})$ arising from the first term. We wish to show that each of the terms in (25) is linear in $Z$. Let us first consider terms involving the orbital energies. We extend the idea of Linderberg and Shull and expand the one-electron orbital energies $\eta$ in powers of $Z$.

$$\begin{aligned}\eta_{2s}&=a_1Z^2+b_1Z+c_1+\cdots,\\ \eta_{2p}&=a_2Z^2+b_2Z+c_2+\cdots\,.\end{aligned} \tag{26}$$

In the $R_4$ approximation, only the leading term is nonzero and $a_1=a_2$. As we have seen, $\eta_{2s}\neq\eta_{2p}$, and the $R_4$ approximation can not be used for the terms involving the $\eta_{2s}$, $\eta_{2p}$. It is necessary to include terms in (26) beyond the leading one. If we now continue to assume that $a_1=a_2$ as is the case in the $R_4$ approximation, retain the linear terms, but drop all succeeding terms, we would have

$$\begin{aligned}\eta_{2s}&=aZ^2+b_1Z\\ \eta_{2p}&=aZ^2+b_2Z.\end{aligned} \tag{27}$$

Since the coefficients of $\eta_{2s}$ and $\eta_{2p}$ are equal in Eq. (25), the quadratic contribution becomes zero and thus the terms involving $\eta_{2s}$, $\eta_{2p}$ in (25) are linear in $Z$. Since in our approximation the $F$ and $G$ parameters are linear in $Z$ and the two-electron term $\tau$ is a linear combination of $F$ and $G$ parameters, the remaining terms in (25) are linear in $Z$. We are justified in assuming that the Hartree-Fock Coulomb and exchange integrals have approximately the same $Z$ dependence as the hydrogen ones, since we found in paper I that the use of the model $\sum 1/r_{ij}$ potential in $R_4$ gave equally good results for hydrogen and Hartree-Fock orbitals. Since strict $Z$-dependence is a property of $R_4$ symmetry our assumption seems reasonable. By treating our calculation as a perturbation of an exactly $R_4$ symmetrical problem, the hydrogen atom, we are able to derive the linear $Z$ dependence of the $\epsilon(2s^2)$ nondynamical correlation for a model much closer than hydrogen to the real atom.

The $Z$ dependence of the $R_4$ calculated $\epsilon(2s^2)$ correlation energy compared with the values calculated separately for each $Z$ by means of configuration interaction is given in Table IV. We see that the $Z$ dependence for the actual values is approximately linear. Furthermore the agreement between the correlation energies calculated by means of $R_4$ and by configuration interaction improves as $Z$ increases. As $Z$ increases the $2s$ and $2p$ levels in atoms become more nearly degenerate and the $R_4$ approximation of the hydrogen-like degeneracy becomes more valid. In addition, from a consideration of the Layzer expansion[3] of the energy in inverse powers of $Z$, it is clear that increasing $Z$ decreases the importance of the larger inverse powers that were neglected in the argument for linear $Z$-dependence of the $\epsilon(2s^2)$ correlation energy.

The dependence of $\epsilon(2s^2)$ on $N$, the number of electrons, can be understood by means of the exclusion principle. In the language of the "many-electron theory,"[2] the exclusion principle imposes "orbital orthogonality" conditions on the correlation wave function,[2] i. e., $\langle u_{ij}\,|\,k\rangle=0$. Thus for Be the correlation wave function is

$$\begin{aligned}\hat{u}_{34}=c_1[&\mathcal{B}(2p_+2\bar{p}_-)-\mathcal{B}(2\bar{p}_+2p_-)\\ &-\mathcal{B}(2p_0 2\bar{p}_0)]\,;\end{aligned} \tag{28}$$

for B:

$$\hat{u}_{34}=c_2[\mathcal{B}(2p_+2\bar{p}_-)-\mathcal{B}(2\bar{p}_+2p_-)]\,; \tag{29}$$

for C:

$$\hat{u}_{34}=c_3[\mathcal{B}(2p_+2\bar{p}_-)]; \tag{30}$$

TABLE IV. $Z$ dependence of $\epsilon(2s^2)$ nondynamical correlation energy (in eV).

| $Z$ | $-\epsilon(2s^2)_Z$ calculated using $R_4$ | $-[Z/(Z-1)]\epsilon(2s^2)_{Z-1}$ | $-\epsilon(2s^2)_Z$ calculated by McKoy & Sinanoğlu[6] | $-[Z/(Z-1)]\epsilon(2s^2)_{Z-1}$ |
|---|---|---|---|---|
| | | Be $^1S$ isoelectronic sequence | | |
| 4 | 1.22 | 1.22 | 1.132 | |
| 5 | 1.52 | 1.52 | 1.417 | 1.415 |
| 6 | 1.83 | 1.83 | 1.828 | 1.70 |
| 7 | 2.13 | 2.13 | 2.309 | 2.13 |
| 8 | 2.44 | 2.44 | 2.554 | 2.63 |
| 9 | 2.74 | 2.74 | 2.906 | 2.87 |
| 10 | 3.05 | 3.05 | 3.248 | 3.22 |
| | | B $^2P$ isoelectronic sequence | | |
| 5 | 0.870 | 0.870 | 0.811 | |
| 6 | 1.045 | 1.045 | 1.069 | 0.973 |
| 7 | 1.219 | 1.219 | 1.270 | 1.247 |
| 8 | 1.393 | 1.393 | 1.477 | 1.429 |
| 9 | 1.567 | 1.567 | 1.692 | 1.662 |
| 10 | 1.741 | 1.741 | 1.882 | 1.880 |
| | | C $^3P$ isoelectronic sequence | | |
| 6 | 0.503 | 0.503 | 0.457 | |
| 7 | 0.587 | 0.587 | 0.563 | 0.533 |
| 8 | 0.671 | 0.671 | 0.656 | 0.633 |
| 9 | 0.754 | 0.754 | 0.745 | 0.738 |
| 10 | 0.838 | 0.838 | 0.832 | 0.828 |

and it is zero for the ground states of the other first-row atoms.[5] The exclusion principle manifests itself just as clearly using the $R_4$ approach. Table I of paper I shows that for N $^4S$, F $^2P$, and Ne $^1S$ there is only one state of the proper symmetry. For O $^3P$ there are two states (111) and (1 − 1 1), but these states are degenerate and do not mix. Thus for these atoms there is no $2s^2$ nondynamical correlation.

Let us now look at the atoms with nonzero $2s^2$ correlation energy. We see that $\hat{u}_{34}$ for Be, B, and C have successively three, two, and one terms. If we assume that each of these terms contributes roughly the same amount to the correlation energy as is reasonable from symmetry considerations, it is clear that the nondynamical correlation energy will decrease from Be to B to C. To a first approximation we take this dependence on $N$ to be given by a term linear in the number of $p$ electrons in the ground configuration. As the number of $p$ electrons increases, the number of possible excitations of the $2s$ electrons is reduced because of restrictions imposed by the Pauli exclusion principle. These excitations of the $2s$ electrons are responsible for the nondynamical correlation energy. Combining this effect with the linear $Z$ dependence we have

$$\epsilon(2s^2) = Z(a - bN), \tag{31}$$

where $a$ and $b$ are constants and $N$ is the number of $p$ electrons in the ground configuration. For the calculation of $\epsilon(2s^2)$ using $R_4$ we set $a = 0.306$ eV and $b = 0.112$ eV, while for the calculation of McKoy and Sinanoğlu[5] we set $a = 0.300$ eV and $b = 0.112$ eV. We find that Eq. (31) with the appropriate values of $a$ and $b$ gives values for $\epsilon(2s^2)$ correlation energy that agree quite well with those calculated by both the "many-electron theory"[2] and by group-theoretical methods.

## IV. EXTENSION TO SECOND-ROW ATOMS

The methods described above can easily be extended to the second row. We will be concerned with the nondynamical correlation only, since we have seen that the present group-theoretical approach cannot give the actual energy-level separations accurately; the dynamical correlations are left out. The calculation proceeds in exactly the same way as for the first row. We treat in our example the $3s^2\,{}^1S$, $3p^2\,{}^1S$, and $3d^2\,{}^1S$ mixing in magnesium. We subtract out the vacuum and self-energy terms and use $R_4$ to diagonalize the three-by-three configuration-interaction matrix. We find a value of 0.179 a.u. for the lowest eigenvalue, the eigenvalue corresponding to the (400) state. The actual diagonalization gives a value of 0.166 a.u. Putting in the correction for the orbital contribution to the correlation energy we find a value of − 0.031 a.u. for $\epsilon(3s^2)$. This value is in good agreement with the value of − 0.0306 a.u. given by McKoy and Sinanoğlu.[12] We also note that a linear $Z$ dependence for $\epsilon(3s^2)$ correlation energy is predicted for the same reasons as linear $Z$ dependence was explained for the nondynamical correlation in first row atoms. Examination of the McKoy and Sinanoğlu results show that this prediction is borne out fairly well.

## V. CONCLUSION

We have seen that $R_4$ can be applied to first row atoms to give very good approximations to the values of nondynamical correlation energy. In addition the $Z$ dependence and the role of the exclusion principle are elucidated. The application to the second row shows that it should be possible to obtain estimates of nondynamical correlation in atoms where values for these quantities are not available.

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# Radiative Capture of Electrons by Chlorine, Bromine, and Iodine Atoms*

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Absolute intensities were measured in the continuous emission spectrum resulting from electron attachment to the halogen atoms in a shock-heated plasma seeded with sodium halides. The intensity measurements were used to determine new photodetachment cross sections for the negative chlorine, bromine, and iodine ions in the wavelength region between 3000 and 4000 Å. These cross sections are presented here and, where possible, are compared with theoretical and experimental values obtained by other methods. For the case in which the halogen atom is left in the ground state ($^2P_{3/2}$), the present experiments give photodetachment cross sections of $1.2 \times 10^{-17}\,\mathrm{cm}^2$ for $\mathrm{Cl}^-$, $2.0 \times 10^{-17}\,\mathrm{cm}^2$ for $\mathrm{Br}^-$, and $2.2 \times 10^{-17}\,\mathrm{cm}^2$ for $\mathrm{I}^-$ near the detachment thresholds.

## I. INTRODUCTION

When a neutral halogen atom captures a free electron to form a negative ion, the excess energy, consisting of the binding energy and the kinetic energy of the electron, may be transferred to a third body (usually another electron), or it may be converted to radiation. The radiative two-body attachment process is considered herein. Because the free electrons in a plasma have a continuous energy distribution corresponding to the electron temperature, the spectrum resulting from electron capture is continuous and has a long-wavelength limit specified by the electron affinity of the atoms. The electron-capture continuum is analogous to the positive-ion recombination continuum extending beyond the convergence limit of a particular line series of a neutral atom. The negative halogen ion, however, exhibits no discrete line spectrum, owing to the absence of any energy levels below the detachment energy. For this reason, the electron-cap-