

Correlation Effects in Atoms

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The applicability of many-body perturbation theory in calculating electron correlations in atoms has been investigated. It was found that, in order for results to agree well with experiment, certain classes of diagrams, representing terms of the perturbation series, must be included to many orders. The higher order diagrams were found to be more important in calculating correlations among the outer electrons than among inner electrons. Methods for summing various classes of these diagrams were found. The total correlation energy in beryllium was calculated by perturbation theory, by the use of an IBM 7090 computer, to be -2.48 ± 0.11 eV. The value obtained from experiment is -2.59 eV. The calculated correlation energies for the different electronic shells were found to be -1.19 eV among $2s$ electrons, -1.15 eV among $1s$ electrons, and -0.135 eV between the $1s$ and $2s$ shells.

I. INTRODUCTION

THE Rayleigh-Schrödinger perturbation theory for many-body systems has been described by Goldstone¹ and is often referred to as Goldstone's perturbation theory. Goldstone has shown that in this theory certain terms containing "unlinked clusters" may be omitted and that the terms for the energy beyond first order are then proportional to the number of particles present. In this description of perturbation theory, annihilation and creation operators are used to account for Fermi-Dirac statistics, and the terms of the expansion are represented by diagrams or graphs similar to the Feynman diagrams of field theory.

Although this perturbation method has been used mainly in solving problems with an infinite number of identical fermions, it is, in principle, quite applicable to other problems and, in particular, to the atomic problem, where a finite number of identical fermions move in the potential field of a nucleus.

This problem is, of course, different from that of an infinite number of fermions, and it is not surprising that terms of the perturbation series which are important in the infinite electron gas problem, for example, are of less importance in the atomic problem, and that other terms assume greater importance. One of the greatest differences in the atomic problem is that the basis states for the perturbation expansion are no longer plane-wave states but are solutions of the Hartree-Fock equations for the atom and are eigenstates of orbital angular momentum. One consequence of this is that the infinite diagrams which were summed by Gell-Mann and Brueckner² in the problem of the (infinite) dense electron gas are now finite and are, in many cases, extremely small.

Another major difference is the importance in the atomic problem of terms in which the exclusion principle is violated in intermediate states. Goldstone¹ has stressed that such terms exist. In the following discussion these terms are denoted as exclusion-principle-violating (EPV) terms.

The purpose of this investigation is to determine the corrections to the Hartree-Fock wave functions and energies for atoms by means of Goldstone's theory. Errors in the Hartree-Fock (HF) wave functions arise from the smearing out or averaging of electronic wave functions in the HF equation. As a result the repulsion between electrons is not accounted for properly. The correlation corrections rectify this deficiency; and the correlation energy is negative because of electron repulsion. This repulsion is not so important for electrons with parallel spins because they are already kept apart by the exclusion principle incorporated into the HF equation by the antisymmetrization of the total wave function. In the perturbation expansion there are exchange diagrams that tend to cancel direct diagrams when the spins of the two interacting electrons are parallel.

The correction for the energy is called the correlation energy and is the difference between the exact eigenvalue E of the Schrödinger equation for N electrons,

$$\left[\sum_{i=1}^N \left(-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j}^N \frac{e^2}{r_{ij}} \right] \psi = E\psi, \quad (1.1)$$

and the exact HF energy, E_{HF} . For atoms of low atomic number Z the difference between E and the total experimental energy E_{exp} is quite small and is due to relativistic effects, which may be estimated. This enables one to compare the calculated correlation energy with the experimental value, as is done for the beryllium atom in Sec. V.

Section II is devoted to a review of many-body perturbation theory. In Sec. III the exclusion-principle-violating diagrams are discussed in detail, and formulas summing these diagrams are derived. Section IV deals with the explicit application of the perturbation theory to atomic systems. The basis states for the expansion are considered in detail, and formulas for the sums over intermediate states are given. In Sec. V the total correlation energy for Be is calculated and found to be in good agreement with the experimental result. The total correlation energy is the sum of the correlations among the various electrons of the atom; correlations

¹ J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957).

² M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

for both the 1s and 2s shells of Be and for the 1s-2s shell interactions are given.

Correlation energies in boron were calculated by use of a screened Coulomb potential, rather than the correct HF potential, to obtain the set of basis states. These results are described in Sec. VI along with an approximate formula for the total correlation energy as a function of the atomic number. The last two sections contain the conclusions (Sec. VII) and Appendix.

II. REVIEW OF GOLDSTONE'S PERTURBATION THEORY

A. Time-Dependent Perturbation Theory

The problem now considered is that of a system of N identical fermions interacting through two-body potentials. The potential between particles i and j is written v_{ij} . There may be also one-body potentials present. The total Hamiltonian for the system is

$$H = \sum_{i=1}^N T_i + \sum_{i < j}^N v_{ij}. \quad (2.1)$$

The symbol T_i is the sum of the kinetic energy for the i th particle and all one-body potentials acting on it. For example, in the atomic problem the one-body potential for the i th electron is its potential energy due to the presence of the nucleus.

The true ground state of the system is ψ_0 , given by

$$H\psi_0 = (E_0 + \Delta E)\psi_0. \quad (2.2)$$

The effect of the N interacting particles may be approximated by a single-particle potential V , and the true system is approximated by an unperturbed system Φ_0 with a total Hamiltonian

$$H_0 = \sum_{i=1}^N (T_i + V_i), \quad (2.3)$$

and the eigenvalue equation³

$$H_0\Phi_0 = E_0\Phi_0. \quad (2.4)$$

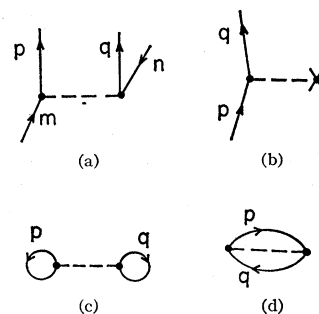
The potential V is required to be Hermitian so that the single-particle wave functions ϕ_n , which are solutions of

$$(T + V)\phi_n = \epsilon_n\phi_n, \quad (2.5)$$

constitute an orthonormal set. The state Φ_0 is a determinant formed from the N solutions of Eq. (2.5) that are lowest in energy. It is assumed that this state is non-degenerate. The states occupied in Φ_0 are called unexcited states. An unoccupied unexcited state is called a hole, and an occupied excited state is called a particle.

³There are essentially three energies in this problem: the unperturbed energy E_0 , the exact energy of the system $E_0 + \Delta E$, and the Hartree-Fock energy E_{HF} , which is E_0 plus the first-order energy term when the potential V is chosen as the Hartree-Fock potential of Eq. (2.14).

FIG. 1. Diagrams associated with matrix elements: (a) $\langle pq|v|mn\rangle$. Particles in the excited state ϕ_m and the unexcited state ϕ_n interact through v and scatter into excited states ϕ_p and ϕ_q , leaving a hole in ϕ_n . (b) $\langle q|V|p\rangle$. A particle in an excited state ϕ_p is scattered by the potential V to the excited state ϕ_q . (c) $\langle pq|v|pq\rangle$. (d) $\langle pq|v|qp\rangle$. Diagrams (c) and (d) represent the interactions of passive unexcited particles.



In the matrix element representation, one has

$$H_0 = \sum_n \epsilon_n \eta_n^\dagger \eta_n \quad (2.6)$$

and

$$H' = H - H_0 = \sum_{p,q,m,n} \langle pq|v|mn\rangle \eta_p^\dagger \eta_q^\dagger \eta_n \eta_m - \sum_{p,m} \langle p|V|m\rangle \eta_p^\dagger \eta_m. \quad (2.7)$$

The η^\dagger and η operators satisfy the usual Fermi-Dirac anticommutation relations. The sums run over all states, unexcited and excited. In the summation, $\sum_{p,q,m,n}$, only distinct matrix elements are included. For example, $\langle pq|v|mn\rangle$ is not distinct from $\langle qp|v|nm\rangle$; however, $\langle pq|v|nm\rangle$ is distinct.

The true ground state is

$$\psi_0 = \lim_{\alpha \rightarrow 0} \frac{U_\alpha(0)\Phi_0}{\langle \Phi_0 | U_\alpha(0) | \Phi_0 \rangle}, \quad (2.8)$$

with

$$\Delta E = \langle \Phi_0 | H' | \psi_0 \rangle, \quad (2.9)$$

where

$$U_\alpha(t) = \sum_{n=0}^{\infty} (-i)^n \int_{t > t_1 > t_2 \dots > t_n} H'(t_1) \dots \times H'(t_n) dt_1 \dots dt_n \quad (2.10)$$

and

$$H'(t) = e^{iH_0 t} H' e^{-iH_0 t} e^{\alpha t}. \quad (2.11)$$

By use of Wick's theorem,⁴ $U_\alpha(0)\Phi_0$ becomes a sum of terms that may be represented by Feynman diagrams or graphs. A particle in an excited state is represented by a line directed upwards, and a hole in an unexcited state is represented by a line directed downwards. The direction of increasing time is upwards. See Fig. 1.

The rules for obtaining $U_\alpha(0)\Phi_0$ are:

(i) Draw all distinct diagrams with no free lines at the bottom.

(ii) For each diagram multiply the v and V matrix elements and the appropriate e^{iEt} and $e^{\alpha t}$ factors and

⁴G. C. Wick, Phys. Rev. **80**, 268 (1950).

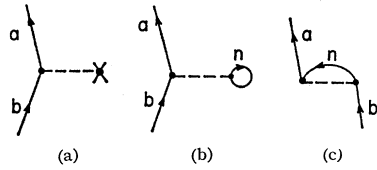


FIG. 2. Diagrams that sum to zero if the Hartree-Fock potential is used to obtain the single-particle states.

include a factor $(-1)^{h+l}$, where h is the number of internal-hole lines and l is the number of closed loops.

(iii) Note that each V has a minus sign with it.

(iv) Attach the pairs of η^\dagger and η operators corresponding to the free (external) lines of each open loop with η^\dagger to the left of η .

(v) Carry out the time integrations and note that the diagrams are time ordered. Goldstone stresses that the exclusion principle is to be ignored in labeling the diagrams.

B. Factorization of Diagrams

Goldstone defines the unlinked part of a diagram as any part completely disconnected from the rest and with no external lines attached. A diagram with no unlinked parts is called linked.

For a given diagram with an unlinked part there are other diagrams in which the interactions of the unlinked parts are in different positions in time relative to the interactions of the linked part. If all these diagrams are summed, the result is that the time integrations of the linked and unlinked parts may be carried out independently. This results in $U_\alpha(0)\Phi_0$ expressed as the product of a sum of linked terms and a sum of unlinked terms. The expression $\langle\Phi_0|U_\alpha(0)|\Phi_0\rangle$ is the sum of all possible unlinked terms and cancels the same factor in $U_\alpha(0)\Phi_0$.

After carrying out the time integrations, one obtains

$$\psi_0 = \sum_L \left(\frac{1}{E_0 - H_0} H' \right)^n \Phi_0, \quad (2.12)$$

where \sum_L means that only linked diagrams are to be included. Also,

$$\Delta E = \sum_{L'} \left\langle \Phi_0 \left| H' \left(\frac{1}{E_0 - H_0} H' \right)^n \right| \Phi_0 \right\rangle, \quad (2.13)$$

where the indicated sum is over connected diagrams with no external lines. The potential V is now chosen to be the Hartree-Fock potential. Thus,

$$\langle a|V|b\rangle = \sum_{n=1}^N (\langle an|v|bn\rangle - \langle an|v|nb\rangle). \quad (2.14)$$

The sum is over the N unexcited states. The sum of the diagrams of Fig. 2 is now zero except for unexcited states $a=b$. When $a=b$, unexcited, the diagrams of Fig. 2 represent the first-order energy term

$$\langle\Phi_0|H'|\Phi_0\rangle = -\frac{1}{2} \sum_{n=1}^N \langle n|V|n\rangle. \quad (2.15)$$

To first order, then, the energy is given by

$$E_{\text{HF}} = \sum_{n=1}^N (\langle n|T|n\rangle + \frac{1}{2}\langle n|V|n\rangle), \quad (2.16)$$

which is the Hartree-Fock result.

III. EXCLUSION-PRINCIPLE-VIOLATING DIAGRAMMS

A. EPV Diagrams Arising from the Linked-Cluster Formula

In applying the perturbation theory to the beryllium atom it was found that certain terms that violate the exclusion principle in intermediate states are numerically significant. In fact, they are the most important terms in third- and higher order energy diagrams and must be considered if good numerical values for the correlation energies are desired. These exclusion-principle-violating (EPV) diagrams are important in finite systems, but in extended systems where the basis states are plane waves these diagrams may be neglected as the volume and density approach infinity.

The EPV diagrams arise from two sources. The first source to be discussed is the factorization of the $U_\alpha(0)\Phi_0$ diagrams into products of linked and unlinked diagrams. The second source of EPV diagrams is the use of the Hartree-Fock potential, and this is discussed in Sec. IIIB.

Goldstone¹ has shown that in order to factor a given diagram with an unlinked part into the product of the linked part times the unlinked part, it is necessary that the interactions of the unlinked part have all possible time orderings relative to the linked part. For example, consider the diagrams shown in Fig. 3. In order to make the factorization shown in Fig. 3(c), it is necessary to include the diagram shown in Fig. 3(b) as well as that of Fig. 3(a). The diagram of Fig. 3(a) vanishes unless the states p, q, r , and s are all included in the unperturbed state Φ_0 . If, however, p, q, r , and s are not all different, then the diagram of Fig. 3(b) vanishes because of the exclusion principle. If $p=q$ and $r=s$, then the diagram of Fig. 3(b) may be added and subtracted and the factorization may still be made, but a negative diagram remains after the factorization has taken place. Goldstone states that such diagrams arise from the application of Wick's theorem and that after the factorization, exclusion-principle-violating diagrams that represent important physical effects remain.

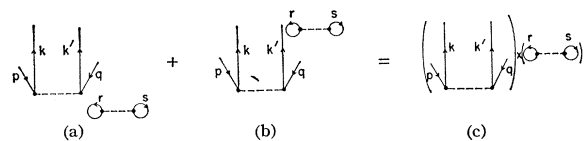


FIG. 3. Factorization of diagrams into the product of a linked and an unlinked diagram. Diagrams (a) and (b) combine to give the product shown in (c).

At this point it is instructive to consider the contraction of the annihilation and creation operators associated with the diagram of Fig. 3(b) when $p=r$ and $q=s$:

$$\langle pq|v|pq\rangle\langle kk'|v|pq\rangle\eta_p^\dagger\eta_q^\dagger\eta_q\eta_p\eta_k^\dagger\eta_{k'}^\dagger\eta_q\eta_p. \quad (3.1)$$

These operators may be contracted in four different ways and the resulting diagrams are shown in Fig. 4. Since each internal-hole line contributes a factor (-1) and each closed loop a factor (-1) , the diagrams of Figs. 4(a) and 4(d) are positive and those of Figs. 4(b) and 4(c) are negative. It should be remembered that in this theory contractions are defined as follows¹:

$$C(\eta_n\eta_n^\dagger) = 1; \quad \phi_n \text{ excited}$$

and

$$C(\eta_n^\dagger\eta_n) = 1; \quad \phi_n \text{ unexcited.}$$

All other contractions are zero.

Diagrams (b) and (c) of Fig. 4 are cancelled because of the Hartree-Fock definition of the potential V . That is, there are diagrams resulting from factorizations similar to that of Fig. 3 that cancel Figs. 4(b) and 4(c). These additional factorizations have unlinked parts with interactions of states ϕ_p and ϕ_q with the potential V and with the other unexcited states. The diagram of Fig. 4(a) is used in the factorization of the unlinked part and only the diagram of Fig. 4(d) remains. It is a linked diagram with one hole-hole interaction. It is readily seen that this diagram violates the exclusion principle because holes are created in the states ϕ_p and ϕ_q , then one more hole is created in each of these states, and then the first two holes are filled. The exclusion principle is violated when the second two holes are created.

A similar examination of the next order in the perturbation expansion yields a diagram with two hole-hole interactions. The expression for the first-order linked diagram with unexcited states ϕ_p and ϕ_q is

$$\sum_{k,k'} \frac{1}{(E_0 - H_0)} \langle kk'|v|pq\rangle\eta_k^\dagger\eta_p\eta_k^\dagger\eta_q. \quad (3.2)$$

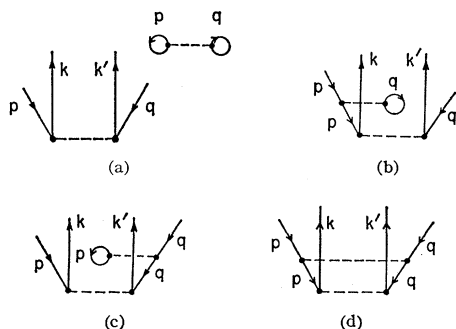


FIG. 4. The four diagrams resulting from the contractions of Eq. (3.1).

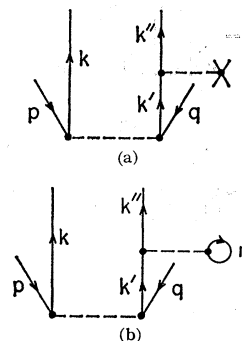


FIG. 5. (a) Scattering by the Hartree-Fock potential. (b) Diagram causing partial cancellation of the diagram shown in (a).

The expression for Fig. 4(d) is

$$\sum_{k,k'} \frac{1}{(E_0 - H_0)} \langle pq|v|pq\rangle \times \frac{1}{(E_0 - H_0)} \langle kk'|v|pq\rangle\eta_k^\dagger\eta_p\eta_k^\dagger\eta_q. \quad (3.3)$$

In both the above expressions, the denominator is

$$E_0 - H_0 = \epsilon_p + \epsilon_q - \epsilon_k - \epsilon_{k'},$$

where ϵ_n is the energy for the state ϕ_n . The next higher order expression due to hole-hole interactions is obtained by multiplying by the factor

$$\frac{1}{E_0 - H_0} \langle pq|v|pq\rangle.$$

Since, for these diagrams, $(E_0 - H_0)$ always has the same value, the sum of all such diagrams is a geometric sum that converges provided

$$\langle pq|v|pq\rangle(E_0 - H_0)^{-1} < 1.$$

The result is that the sum to all orders of EPV diagrams due to hole-hole interactions is given by

$$\sum_{k,k'} \frac{1}{(E_0 - H_0 - \langle pq|v|pq\rangle)} \langle kk'|v|pq\rangle\eta_k^\dagger\eta_p\eta_k^\dagger\eta_q. \quad (3.4)$$

Since there may be also hole-hole EPV diagrams involving exchange, the denominator of Eq. (3.4) should be replaced by

$$(E_0 - H_0 - \langle pq|v|pq\rangle + \langle pq|v|qp\rangle). \quad (3.5)$$

In the applications of this theory discussed in later sections, the quantity

$$(\langle pq|v|pq\rangle - \langle pq|v|qp\rangle)(E_0 - H_0)^{-1}$$

is always less than one and so the summation is valid. The quantity $(E_0 - H_0)$ is always negative, since Φ_0 is the unperturbed ground state of the system. The direct matrix element $\langle pq|v|pq\rangle$ is positive and is, in general, much larger than the exchange term for the

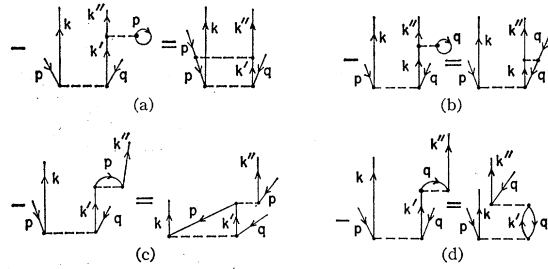


FIG. 6. Diagrams resulting from the interaction of an excited particle with the Hartree-Fock potential after the cancellation of all diagrams with passive unexcited particles. Diagrams (a) and (b) are hole-particle EPV diagrams. Diagrams (c) and (d) are the corresponding exchange terms.

applications to be considered. The resulting denominators are then always negative and never zero in these cases. In all further discussions of diagrams the energy denominators are assumed shifted to account for EPV hole-hole interactions to all orders. The origin of the EPV hole-hole diagrams may be demonstrated also by invoking the Hartree-Fock cancellation before the factorizations. All EPV diagrams may be factored into products of linked EPV diagrams and unlinked diagrams when higher orders are considered. When third-order terms, for example, are investigated, there will be factorizations similar to that shown in Fig. 3(c) but with the linked part of Fig. 3(c) replaced by the linked diagram of Fig. 4(d).

B. EPV Diagrams Arising from the Hartree-Fock Cancellation

In using this perturbation theory it seems natural to ask whether all states should be determined with a fixed potential, since the effective potential may be changed by excitations. In fact, the effect of the changed potential is accounted for by the existence of a certain class of diagrams now described.

Consider the diagram of Fig. 5(a). This diagram is cancelled by diagrams of the type shown in Fig. 5(b) and the corresponding exchange diagrams, provided the state ϕ_n ranges over all the unexcited states. This, of course, does not happen because the states ϕ_p and ϕ_q are no longer occupied and so the cancellation is incomplete. This difficulty is removed by adding and subtracting the necessary diagrams to complete the cancellation. The remaining subtracted diagrams are shown in Fig. 6. Note that in diagrams (a), (b), and (d) of Fig. 6 the minus sign on the left is accounted for by the hole line on the right. In Fig. 6(c) the minus sign is accounted for by the rule that the η^\dagger and η operators for the free lines of each open loop go together with η^\dagger to the left of η . The diagram of Fig. 6(c) can exist only when states ϕ_p and ϕ_q have parallel spins. In this order of perturbation theory there are also four additional diagrams resulting from the interaction of the particle in the state ϕ_k with the potential V . These results may be obtained also by consideration of the

contractions of the annihilation and creation operators. Diagrams of the type described have been found to be very important in calculating correlations in Be, particularly among the outer electrons.

C. Higher-Order EPV Diagrams

Another class of EPV diagrams arising from the factorization into products of linked and unlinked diagrams is illustrated in Fig. 7. After the factorization of the leftmost diagram, there are two remaining diagrams shown on the right. Ultimately, of course, these too will acquire similar factors when higher orders are considered, as did the simple diagram on the left. As Goldstone showed, all these unlinked diagrams are cancelled by the factor $\langle \Phi_0 | U_a(0) | \Phi_0 \rangle$ in the denominator of ψ_0 . The drawing of these two subtracted diagrams as shown does not mean that they may be considered as having unlinked parts as defined in Ref. 1. The method of subtracting diagrams in order to achieve factorizations often gives simpler results than the contraction of operators and it also enables one to keep in mind orders of magnitudes of higher order diagrams when the sizes of the component parts are known. If the contraction of operators is employed, then $-Y1$ and $-Y2$ of Fig. 7 are each replaced by three complicated linked diagrams of equal magnitudes but with different signs.

The expression for the first of the subtracted diagrams of Fig. 7 is (omitting the η^\dagger and η operators)

$$Y1 = \sum_{kk'k''k'''} \frac{1}{D(k'',k''')} \langle pq|v|kk' \rangle \frac{1}{D(k,k') + D(k'',k''')} \times \langle k''k'''|v|pq \rangle \frac{1}{D(k,k')} \langle kk'|v|pq \rangle, \quad (3.6)$$

where

$$D(k,k') = \epsilon_p + \epsilon_q - \epsilon_k - \epsilon_{k'} - \langle pq|v|pq \rangle + \langle pq|v|qp \rangle. \quad (3.7)$$

The sum of all hole-hole EPV diagrams is implied in Fig. 7 and is reflected in the shifted denominators of Eq. (3.7).

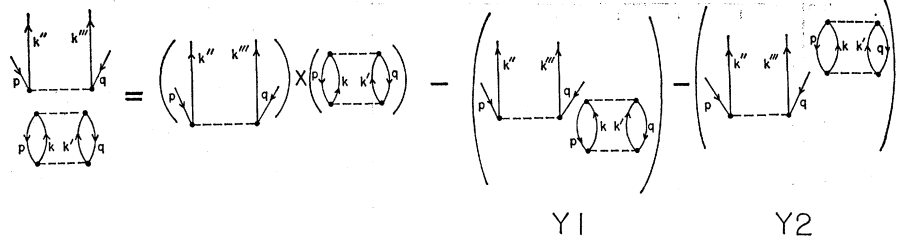
The expression for $Y2$ of Fig. 7 is

$$Y2 = \sum_{kk'k''k'''} \frac{1}{D(k'',k''')} \langle pq|v|kk' \rangle \frac{1}{D(k,k') + D(k'',k''')} \times \langle kk'|v|pq \rangle \frac{1}{D(k'',k''')} \langle k''k'''|v|pq \rangle. \quad (3.8)$$

Again, the annihilation and creation operators are implied. The matrix elements $\langle kk'|v|pq \rangle$ are, in general, significant only over a limited range of the excited states k and k' . For many problems it is a good approximation to replace Eqs. (3.6) and (3.8) by

$$Y1 \approx Y2 \approx \frac{1}{2} \gamma \sum_{kk'k''k'''} \frac{1}{D(k'',k''')} \langle k''k'''|v|pq \rangle E_2(pq), \quad (3.9)$$

FIG. 7. Factorization of an unlinked diagram resulting in two EPV diagrams on the right. The two subtracted diagrams may not be considered as unlinked in this case.



where

$$\gamma = E_2^{(2)}(p, q) / E_2(p, q), \quad (3.10)$$

$$E_2(p, q) = \sum_{kk'} \langle pq | v | kk' \rangle \frac{1}{D(k, k')} \langle kk' | v | pq \rangle, \quad (3.11)$$

and

$$E_2^{(2)}(p, q) = \sum_{kk'} \langle pq | v | kk' \rangle \frac{1}{[D(k, k')]^2} \langle kk' | v | pq \rangle. \quad (3.12)$$

In the applications to Be such terms as Eq. (3.9) are negligible for correlations among the inner electrons but are significant (of order 10%) for the outer-electron correlations. For the outer electrons the energy denominators are dominated by $\epsilon_p + \epsilon_q - \langle pq | v | pq \rangle$ and the approximations in Eq. (3.9) are valid.

The quantity $L_n(p, q)$ is now defined as any linked diagram of n th order with only two external-hole lines, referring to states ϕ_p and ϕ_q . There may be many internal-hole lines but these also are restricted to states ϕ_p and ϕ_q . The quantity $E_n(p, q)$ is the sum of all energy diagrams of n th order in which the hole lines are restricted to states ϕ_p and ϕ_q . Hole-hole EPV diagrams are considered summed, and this discussion does not include them. For example, $L_1(p, q)$ is given by Eq. (3.4) with the denominator of (3.4) replaced by (3.5); $E_2(p, q)$ (excluding exchange) is given by Eq. (3.11).

By use of Eq. (3.9), the two subtracted diagrams on the right of Fig. 7 give $-\gamma L_1(p, q) E_2(p, q)$. The term $L_1(p, q)$ is replaced now by

$$L_1(p, q) [1 - \gamma E_2(p, q)]. \quad (3.13)$$

Further investigation shows that $L_1(p, q)$ is modified, to a good approximation, by the factor $[1 - \gamma S(p, q)]$, where

$$S(p, q) = \sum_{m=2}^{\infty} E_m(p, q) \times \{1 - \gamma S(p, q) [1 - \gamma S(p, q)]^2\}^{m+1}. \quad (3.14)$$

Although Eq. (3.14) appears to be a difficult expression for $S(p, q)$, the quantity $S(p, q)$ is very nearly the correlation energy $E_{\text{corr}}(p, q)$ between two particles in the state ϕ_p and ϕ_q and is generally small. Equation (3.14) may be replaced by

$$S(p, q) \approx E_{\text{corr}}(p, q) [1 - \gamma E_{\text{corr}}(p, q)]^2. \quad (3.14a)$$

Often $E_{\text{corr}}(p, q)$ may be estimated by physical arguments or on the basis of previous calculations.

For the $2s$ states of Be, $E_{\text{corr}}(2s, 2s) \approx -0.043$ a.u. and $\gamma = -0.789$ a.u.⁻¹.

The linked term $L_m(p, q)$ is modified to

$$L_m(p, q) [1 - \gamma S(p, q)]^m. \quad (3.15)$$

These results are due to EPV diagrams resulting from factorizations in which the unlinked part is second order or higher. The corresponding modification for energy diagrams is

$$E_{m,i}(p, q) \rightarrow E_{m,i}(p, q) [1 - \gamma S(p, q)]^{m-1}, \quad (3.16)$$

where $E_{m,i}(p, q)$ is the i th energy diagram of order m with hole lines referring to ϕ_p and ϕ_q . Equations (3.14), (3.15), and (3.16) are justified in the Appendix.

IV. USE OF PERTURBATION THEORY IN ATOMIC SYSTEMS

A. The Hartree-Fock Potential and Single-Particle States

In making use of Goldstone's perturbation theory¹ it is necessary first to obtain a complete set of single-particle states determined by a potential V . Because of the cancellation of the diagrams of Fig. 2, a great simplification in the number and types of diagrams to be considered results when V is chosen to be the Hartree-Fock (HF) potential. In the matrix-element representation the self-consistent HF potential V is defined by Eq. (2.14). In Eq. (2.14) states $|a\rangle$ and $|b\rangle$ may be any two states of the basis set. The potential v is the Coulomb potential between any two of the interacting particles:

$$v_{ij} = e^2 / r_{ij}. \quad (4.1)$$

The electron states ϕ_n are determined by the eigenvalue Eq. (2.5). In Eq. (2.5), one has

$$T = -\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r}. \quad (4.2)$$

The second term of Eq. (4.2) is the electron's potential energy with the nucleus of atomic number Z . The distance from the electron to the nucleus is r , and e and m are the electronic charge and mass, respectively. Atomic units⁵ are now chosen in which $e = 1$, $m = 1$, and

⁵ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 5.

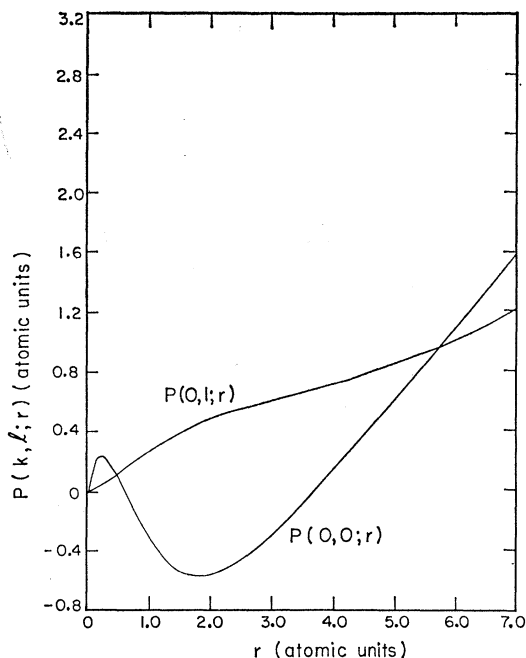


FIG. 8. Behavior of $P(k, l; r)$ for $\epsilon=0$ in the potential field of a neutral beryllium atom. There are no bound $l=1$ states, since $P(0, 1; r)=0$ only at $r=0$. There are two bound $l=0$ states since $P(0, 0; r)$ equals zero at two values of $r \neq 0$.

$\hbar=1$. Energies are expressed in atomic units (a.u.): 1 a.u.=27.210 eV.

Equations (2.5) and (2.14) constitute the self-consistent Hartree-Fock equations. The usual form for Eq. (2.5) in configuration space is

$$\begin{aligned} & -\frac{\nabla^2}{2}\phi_n(\mathbf{r}) - \frac{Z}{r}\phi_n(\mathbf{r}) + \left(\sum_{j=1}^N \int \frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \right) \phi_n(\mathbf{r}) \\ & - \sum_{j=1}^N \left(\delta(m_{sn}, m_{sj}) \int \frac{\phi_j^*(\mathbf{r}')\phi_n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r}) \right) \\ & = \epsilon_n \phi_n(\mathbf{r}), \quad (4.3) \end{aligned}$$

where m_{sn} is the spin projection of the electron in state ϕ_n .⁶ The N Hartree-Fock solutions ϕ_n of lowest energy are determined by solving a set of N -coupled integro-differential equations, Eq. (4.3). These N states determine the potential. Additional states ϕ_n are obtained from Eq. (4.3), and it is not necessary to consider a set of coupled equations for them because they are calculated in the potential field of the N states of lowest energy. Since the HF potential V as written in Eq. (2.14) is Hermitian, an infinite set of orthonormal states comes from Eq. (4.3).⁶ The N lowest in energy constitute the ground state and are called "unexcited states." All other states are called "excited." There is a

tendency for excited states of the perturbation expansion to be confused with true excited states of the total system. It should be remembered that the excited states in this theory are the solutions to the HF equation that are orthonormal to the N unexcited states. These excited states are not true physical states of any system, although they may be given a certain physical interpretation.

B. The Excited States

Consider now the expectation values of the HF potential V as given by Eq. (2.14). If $|a\rangle = |b\rangle$, there are two possibilities. First, $|a\rangle$ may be one of the N unexcited states. In this case when the summation over unexcited states is made in Eq. (2.14), there will be a term for which $|n\rangle = |a\rangle$. The exchange term then cancels the direct term and the resulting sum gives only $N-1$ direct terms in addition to the exchange terms. If $|a\rangle$ is one of the excited states, however, there is no cancellation due to the equality of a direct and an exchange term, and there are N direct terms included in the expectation value of the potential. The physical interpretation is that the potential for an unexcited state is due to the $N-1$ other electrons of the system. The potential for an excited state contains N direct terms and represents interactions with all N particles present in the ground state. One consequence is that in a neutral atom the excited states are determined by a total potential in which the net charge is zero. This, in turn, presents the possibility that for such a potential there may be no bound excited states for the perturbation theory.

The problem as to whether bound, excited, perturbation theory states will occur for neutral atoms is similar to that of the formation of negative ions. For neutral atoms the excited states are determined in the potential field of a nucleus of charge $+N$ and N electrons. The N states that determine this potential are fixed and not affected by the excited state. In the formation of a negative ion, however, the original N states are changed by the presence of the additional electron and are rearranged so as to minimize the energy. Values of the electron affinities in eV are listed by Massey for neutral atoms.⁷ He states that hydrogen has a relatively high affinity of 0.74 eV. Beryllium, for example, has an affinity of 0.2 eV. However, calculations by Hylleraas show that the undisturbed potential of the neutral hydrogen atom is too weak for the existence of a bound state.⁸ It is expected that many other neutral atoms, especially those with lower electron affinities, will behave similarly. If bound states do exist for a neutral atom, there should be very few.

Whenever calculations are made on a particular atom, there still should be a search for bound excited

⁶ J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, Chap. 17, p. 6.

⁷ H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1950), 2nd ed., p. 19.

⁸ E. A. Hylleraas, *Z. Physik* **60**, 624 (1930).

states. One way is to consider the Schrödinger equation as written in Eq. (4.4):

$$\frac{d^2}{dr^2}P(k,l;r) = \frac{l(l+1)}{r^2}P(k,l;r) + 2V(r)P(k,l;r) - 2\epsilon P(k,l;r). \quad (4.4)$$

The function $P(k,l;r)$ is $rR(k,l;r)$, where $R(k,l;r)$ is the radial part of the wave function with angular momentum l and energy $\epsilon = k^2/2$. The usual separation of the wave function into angular and radial parts is assumed. Attractive potentials $V(r)$ pull the wave function toward the r axis. The attraction is enhanced by the energy term for $\epsilon > 0$. For $\epsilon = 0$, the behavior of $P(k,l;r)$ indicates the number of bound states of angular momentum l for the potential $V(r)$. The functions $P(0,0;r)$ and $P(0,1;r)$ for Be are shown in Fig. 8. Since $P(0,0;r)$ fails to turn over a third time, the potential cannot support a $3s$ bound state and the only bound states for $l=0$ are the P_{1s} and P_{2s} unexcited states. There are no bound $l=1$ states, since $P(0,1;r)$ does not turn over.

It may be argued that the exchange part of the potential is different for different energies and that the failure of the wave function to turn over at zero energy does not guarantee the absence of a bound state. This is true, but it seems most unlikely that the difference in exchange contributions for zero energy and near-zero energy is sufficient to cause a bound state.

Another way to look for bound states is to make use of Levinson's theorem,⁹ which relates the number of bound states for a potential $V(r)$ to the phase shifts $\delta_l(k)$ at zero and infinite energies. According to Levinson's theorem, if the potential $V(r)$ satisfies

$$\int_0^\infty dr \, r |V(r)| < \infty \quad (4.5)$$

and

$$\int_0^\infty dr \, r^2 |V(r)| < \infty,$$

then n_l , the number of bound states of angular momentum l , is given by

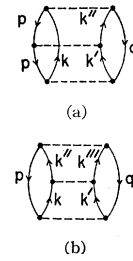
$$\pi n_l = \delta_l(0) - \delta_l(\infty). \quad (4.6)$$

Conditions (4.5) are clearly satisfied by the potentials of neutral atoms. For Be, $\delta_0(0) = 2\pi$, and all other phase shifts at zero and infinite energies are zero. The value 2π for $\delta_0(0)$ is seen in Fig. 8, where $P(0,0;r)$ undergoes a complete cycle. Jauch has shown¹⁰ that Eq. (4.6) is a simple consequence of the orthogonality and completeness relation for the set of eigenfunctions of the total-energy operator $H = H_0 + V$. He states that this is a property that must be assumed to hold for any reasonable quantum-mechanical system.

⁹ R. G. Newton, J. Math. Phys. **1**, 319 (1960).

¹⁰ J. M. Jauch, Helv. Phys. Acta **30**, 143 (1957).

FIG. 9. Third-order energy diagrams with transitions between excited states. (a) EPV hole-particle diagram. (b) Ladder diagram. Two particles in excited states interact and scatter into two new excited states.



In Goldstone's theory the limitation to nondegenerate ground states is a restriction to systems in which the energy denominators $(E_0 - H_0)$ cannot vanish for excited states of the perturbation theory. This requirement is certainly met in atomic systems even though the ground state may be degenerate in the usual sense.

C. Wave Functions for Continuum States

In determining the form of the continuum ($\epsilon > 0$) states it is necessary to consider the Hartree-Fock potential of Eq. (2.14). For those atoms that do not have spherical symmetry in their electron distributions, this HF potential is not a central potential, and the eigenstates of Eq. (4.3) are not eigenstates of orbital angular momentum l . It is expected, however, that it is a good approximation to make a spherical average so that the excited states are eigenstates of l . This may be accomplished by multiplying Eq. (4.3) by the appropriate spherical harmonic and integrating over all angles. For Be, which has spherical symmetry, no approximation is necessary. It was chosen for the numerical calculations in order that any discrepancies between calculated and experimental results might be linked directly to the perturbation series.

An additional complication arises from the fact that the potential of Eq. (2.14) is the unrestricted Hartree-Fock (UHF) potential in which states with identical quantum numbers except for spin may have different radial wave functions and energies. An example is the lithium atom with two $1s$ electrons and one $2s$ electron. The $1s$ electron with spin parallel to that of the $2s$ electron has an exchange potential term with the $2s$ electron. The other $1s$ electron does not have this exchange term and so the two $1s$ radial orbitals differ. The situation is similar for excited states, and so it may be necessary to determine excited states of spin up and spin down. Again, Be does not have this complication.

The continuum states $|k,l,m,m_s\rangle$ are determined by Eq. (4.3) with $\epsilon = k^2/2$. Spherical symmetry is assumed so that

$$\langle \mathbf{r} | k,l,m,m_s \rangle = R(kl;r) Y_{lm}(\theta,\phi) X_s(m_s). \quad (4.7)$$

In Eq. (4.7), r, θ, ϕ are spherical coordinates, l and m are the orbital angular momentum and azimuthal quantum number, respectively, and m_s is the spin projection. The spin eigenfunction is $X_s(m_s)$. The state

$|k, l, m, m_s\rangle$ is now written as $|k\rangle$, where the remaining quantum numbers are implied.

Consider the atom enclosed in a large spherical volume of radius R_0 that tends to infinity. At distances far from the atom the potential is effectively zero (for neutral atoms), and the radial solutions $R(kl; r)$ to Eq. (4.3) are linear combinations of $j_l(kr)$ and $n_l(kr)$, the spherical Bessel and Neumann functions.¹¹ As $r \rightarrow \infty$,

$$R(kl; r) \sim \cos \frac{[kr + \delta_l - \frac{1}{2}(l+1)\pi]}{kr}. \quad (4.8)$$

Since $\int_0^\infty dr r^2 R^2(kl; r) = 1$, the normalization is $(2/R_0)^{1/2}k$, and

$$R(kl; r) = \left(\frac{2}{R_0}\right)^{1/2} \cos \frac{[kr + \delta_l - \frac{1}{2}(l+1)\pi]}{r}. \quad (4.9)$$

Since the wave function must vanish on the boundary R_0 ,

$$kR_0 + \delta_l - \frac{1}{2}(l+1)\pi = n\pi, \quad (4.10)$$

where n is an integer. The number of eigenstates Δn for fixed l in the range Δk is determined by

$$\Delta k R_0 + \Delta \delta_l = \Delta n \pi. \quad (4.11)$$

Since $(\Delta \delta)R_0^{-1} \rightarrow 0$ for finite Δk , it follows that

$$\Delta n = (R_0/\pi)\Delta k \quad (4.12)$$

and

$$\sum_k = \frac{R_0}{\pi} \int_0^\infty dk. \quad (4.13)$$

In calculating energy diagrams, every state that is excited is in turn de-excited. It is possible then to replace \sum_k by $(2/\pi)\int_0^\infty dk$, provided the normalization factor $(2/R_0)^{1/2}$ is dropped from $R(kl; r)$ in Eq. (4.9). Sums over intermediate states involve sums over l , m , and m_s in addition to $\int_0^\infty dk$. When sums over m values are made for excitations, it is found that the resulting intermediate state has the same orbital momentum as the initial state. This is expected since the total angular-momentum operator commutes with the perturbation $(r_{ij})^{-1}$.

Consider the diagram of Fig. 9(a) which is a hole-particle EPV energy diagram. In calculating diagrams of this type in the atomic problem, the intermediate matrix element $\langle pk'' | v | pk' \rangle$ can become infinite for $k' = k''$ as $R_0 \rightarrow \infty$, but the integrations over k' and k'' remove the infinity. In making numerical calculations it is a practical necessity to truncate the integrations at some finite R_0 , and the resulting error $\epsilon 1$ is given approximately by

$$\epsilon 1 \approx \left(\int_{R_0}^\infty dr \frac{\sin \mu r}{r^2} \right) E_2^{(2)}(p, q), \quad (4.14)$$

¹¹ L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., pp. 77, 78.

where $E_2^{(2)}(p, q)$ is given by Eq. (3.12). The symbol μ is the value of $|k'' - k'|$ for which the matrix elements begin to show significant errors due to the finite R_0 . The truncation radius R_0 was chosen as 120 a.u. for the calculations of Sec. V. In the diagram of Fig. 9(b), infinities as in Fig. 9(a) arise when $k'' = k$ or $k''' = k'$. When both equalities occur, the infinity is stronger but is again removed by integrations. This error, $\epsilon 2$, is given roughly by

$$\epsilon 2 \approx \int_{R_0}^{R_F} dr \frac{\sin \mu r}{r^2} (\mu r - \mu R_0) E_2^{(2)}(p, q), \quad (4.15)$$

where $R_F \approx 2/\mu$.

V. THE CORRELATION ENERGY OF BERYLLIUM

A. Observed Correlation Energies

The procedures described are equally applicable in obtaining many-body corrections to atomic wave functions and energies. The many-body property most readily determined experimentally is the correlation energy, defined as the difference between the eigenvalue E of the Schrödinger Eq. (1.1) and the exact Hartree-Fock energy E_{HF} :

$$E_{\text{corr}} = E - E_{\text{HF}}. \quad (5.1)$$

The eigenvalue E is the difference between the experimental energy of the atom and the relativistic contributions to the energy, and so

$$E_{\text{corr}} = E_{\text{exp}} - E_{\text{rel}} - E_{\text{HF}}. \quad (5.2)$$

By use of spectroscopic data,¹² $E_{\text{exp}} = -14.6682$ a.u. Fröman¹³ has estimated the relativistic corrections to the Be energy as -0.002 a.u. Calculations by Watson give $E_{\text{HF}} = -14.57299$ a.u. for Be.¹⁴ The value for E_{HF} should be multiplied by the reduced electron mass for Be divided by the electron mass to give $E_{\text{HF}} = -14.57211$ a.u. With the use of these numbers, Eq. (5.2) gives $E_{\text{corr}} = -0.0941$ a.u. A more accurate result may be obtained by use of the spectroscopic data to obtain the first two ionization potentials for Be and then by use of Pekeris' calculations¹⁵ for the non-relativistic energy of Be^{++} . The result is $E_{\text{corr}} = -0.0953$ a.u.¹⁶ The results of calculations reported in this investigation give $E_{\text{corr}} = -0.091$ a.u.

¹² *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I.

¹³ A. Fröman, *Phys. Rev.* **112**, 870 (1958).

¹⁴ R. E. Watson, *Phys. Rev.* **119**, 170 (1960).

¹⁵ C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).

¹⁶ This procedure is that used by Watson in Ref. 14, where he reports $E_{\text{corr}} = -0.0944$ a.u. The small discrepancy between Watson's result and that of this investigation is believed to be due to Watson's conversion factor between atomic units and eV.

B. Second-Order Energy Calculations

The HF ground-state wave functions $P_{1s}(r)$ and $P_{2s}(r)$ of Kibartas and Yutsis¹⁷ were used in the numerical calculations. As explained in Sec. IVB, there are no bound excited states (of the perturbation theory) for Be. The continuum states were obtained by solving Eq. (4.3) on the IBM 7090 computer, using Noumerov's method¹⁸ for the integration. Matrix elements were calculated, and then the appropriate double integrals were performed to obtain second-order energy terms. The results of these calculations are listed in Table I. The unmodified second-order energy term is

$$E_2^0(l; p, q) = \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk \times \int_0^\infty dk' \frac{\langle pq | v | kk'; l \rangle \langle kk'; l | v | pq \rangle}{\epsilon_p + \epsilon_q - \frac{1}{2}k^2 - \frac{1}{2}k'^2}. \quad (5.3)$$

The orbital angular momentum l is identical for each of the states k and k' . A consideration of the expansion $1/|\mathbf{r}_i - \mathbf{r}_j|$ in spherical harmonics¹⁹ shows that both k and k' must have the same l because all unexcited states of Be are $s(l=0)$ states. In addition, the azimuthal quantum numbers m and m' of states k and k' must add to zero. In Eq. (5.3) the sum over l is omitted but the sums over m and m_s are still implied. The second-order term with the modified denominator because of hole-hole EPV diagrams [see Eq. (3.5)] is

$$E_2(l; p, q) = \left(\frac{2}{\pi}\right)^2 \int_0^\infty dk \int_0^\infty dk' \times \frac{\langle pq | v | kk'; l \rangle \langle kk'; l | v | pq \rangle}{\epsilon_p + \epsilon_q - \frac{1}{2}k^2 - \frac{1}{2}k'^2 - \langle pq | v | pq \rangle + \langle pq | v | qp \rangle}. \quad (5.4)$$

For the exchange terms, the first matrix element in both Eqs. (5.3) and (5.4) is changed to $\langle pq | v | k'k; l \rangle$, and the usual minus sign for exchange multiplies the terms. In the numerical calculations for $|pq\rangle = |1s1s\rangle$, the values of k and k' for significant contributions ranged from 0.0 to 10.0 a.u. The significant contributions for $|pq\rangle = |2s2s\rangle$ ranged from $k=0.0$ to $k=1.0$ a.u. It is seen from Table I that the second-order contributions give less than 70% of E_{corr} . Even if the true second-order terms E_2^0 are used, they still fail to give E_{corr} , which is approximately -0.095 a.u., and so it is necessary to consider higher order terms in the perturbation expansion.

¹⁷ V. V. Kibartas and A. P. Yutsis, *Zh. Eksperim. i Teor. Fiz.* **25**, 264 (1953).

¹⁸ M. G. Salvadori and M. L. Baron, *Numerical Methods in Engineering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1961), 2nd ed., Chap. 3, p. 137.

¹⁹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 174.

C. Correlations among 2s Electrons

An investigation of the correlation energies in atoms by means of configuration interaction has been made by Linderberg and Shull.²⁰ They conclude that in many-electron atoms the inner pair of electrons is very similar to the $1s$ pair in the He-like series. For $Z=4$, they report $E_{\text{corr}} = -0.0439$ a.u. for the configuration $1s^2$. Among the outer pair of electrons in Be they found -0.043 a.u. from $l=1$ correlations. Reference to Table I indicates that the second-order results are worse for $2s$ than for $1s$ correlations. Higher order terms for $2s$ correlations are now examined, and it is found that the series converges rather slowly. Convergence is more rapid for the $1s$ terms.

Consider the EPV diagrams of Sec. III B. There are four possible energy diagrams arising from linked diagrams of the types shown in Figs. 6(a) and (b). They arise from interactions of each excited state with each of the unexcited states of the diagram, and they are called hole-particle EPV diagrams. There are two exchange energy diagrams, one corresponding to the linked exchange diagram of Fig. 6(d) and the other to the diagram of Fig. 6(d) in which k replaces k' in the second interaction. All four hole-particle EPV diagrams are numerically equal, since both $2s^+$ and $2s^-$ states have identical wave functions except for spin. Both exchange diagrams are also numerically equal.

The third-order hole-particle EPV diagram is denoted by

$$E_{3\text{hp}}(l; 2s, 2s) = -\left(\frac{2}{\pi}\right)^3 \int_0^\infty dk \int_0^\infty dk' \int_0^\infty dk'' \langle 2s2s | v | kk'' \rangle \times \frac{1}{D(k, k'')} \langle 2sk'' | v | 2sk' \rangle \frac{1}{D(k, k')} \langle kk' | v | 2s2s \rangle, \quad (5.5)$$

where

$$D(k, k') = \epsilon_{2s} + \epsilon_{2s} - \frac{1}{2}k^2 - \frac{1}{2}k'^2 - \langle 2s2s | v | 2s2s \rangle. \quad (5.6)$$

The exchange diagram is denoted

$$E_{3\text{ex}}(l; 2s, 2s) = \left(\frac{2}{\pi}\right)^3 \int_0^\infty dk \int_0^\infty dk' \int_0^\infty dk'' \langle 2s2s | v | kk'' \rangle \times \frac{1}{D(k, k'')} \langle k''2s | v | 2sk' \rangle \frac{1}{D(k, k')} \langle kk' | v | 2s2s \rangle. \quad (5.7)$$

In Eqs. (5.5) and (5.7), the orbital momentum l is implied for intermediate states. The quantity $a(l; 2s, 2s)$ is defined:

$$a(l; 2s, 2s) = E_{3\text{hp}}(l; 2s, 2s) / E_2(l; 2s, 2s), \quad (5.8)$$

²⁰ J. Linderberg and H. Shull, *J. Mol. Spectry.* **5**, 1 (1960).

TABLE I. Second-order energies for Be calculated with normal and shifted denominators.^a

pq	l	$E_2^0(l; p, q)$	$E_2(l; p, q)$	$\sum_{l=0}^2 E_2(l; p, q)$
$1s+1s^-$	0		-0.01152	
$1s+1s^-$	1	-0.02255	-0.02077	
$1s+1s^-$	2		-0.00345	-0.03574
$2s+2s^-$	0	-0.00241	-0.00192	
$2s+2s^-$	1	-0.02228	-0.01605	
$2s+2s^-$	2	-0.00383	-0.00326	-0.02123
$1s2s^b$	0		-0.002033	
$1s2s^b$	1	-0.004991	-0.004719	
$1s2s^b$	2		-0.000612	
$1s2s^c$	0		0.0009899	
$1s2s^c$	1		0.001108	
$1s2s^c$	2		0.00030 ^d	-0.004966
Total				-0.06194

^a All energies listed are in atomic units. According to Ref. 17, $\epsilon_{1s} = -4.7353$, $\epsilon_{2s} = -0.3092$, $\langle 1s1s|v|1s1s \rangle = 2.2731$, $\langle 2s2s|v|2s2s \rangle = 0.3420$, $\langle 1s2s|v|1s2s \rangle = 0.4805$, and $\langle 1s2s|v|2s1s \rangle = 0.0250$.

^b Results listed include a factor of 4 due to four possible electron pairs.

^c These are exchange terms and include a factor of 2 due to the two possible exchange pairs.

^d This number was estimated and not calculated.

where E_2 is defined by Eq. (5.4). The quantity $a(l; 2s, 2s)$ is sometimes written simply a when the arguments of $a(l; 2s, 2s)$ are understood. Now, one defines

$$b(l; 2s, 2s) = E_{3ex}(l; 2s, 2s)/E_2(l; 2s, 2s), \quad (5.9)$$

and it is written as b when the arguments are understood.

A calculation of a and b gave the values

$$a(1; 2s, 2s) = 0.28504$$

and

$$b(1; 2s, 2s) = -0.06158.$$

The ratio of all third-order hole-particle and exchange EPV diagrams to the second-order energy diagram is then $4a+2b=1.0170$ for $l=1$. An examination of the numerical calculations of $E_{3hp}(1; 2s, 2s)$ showed that the effect of the intermediate interaction may be accurately approximated by a constant. That is, the relative magnitude of different k'' excitations after the interaction are very nearly the same as the relative k' magnitudes. This leads to the following approximate equation for $a(l; 2s, 2s)$:

$$a_{app}(l; 2s, 2s) = \left(-\frac{2}{\pi} \int_0^\infty dk' \langle 2sk'|v|2s2s \rangle \frac{1}{D(k, k')} \langle kk'|v|2s2s \rangle \right) / \langle kk''|v|2s2s \rangle. \quad (5.10)$$

Again, the value l is implied for all intermediate states. The values for k and k'' should be chosen as representative values found in the calculation of E_2 . An indication of the validity of Eq. (5.10) may be obtained from Table II.

Since a_{app} differs very little from a over a wide range of excitations, Eq. (5.10) is a good approximation for a . The relatively large value for $4a+2b$ indicates the

necessity of investigating higher order terms and of looking for other third-order diagrams that will effect at least partial cancellations. For every third-order diagram there are four corresponding fourth-order hole-particle E_{4hp} diagrams and two E_{4ex} diagrams. By invoking the relative constancy of these intermediate interactions, the sum of fourth-order terms of the two types considered is $E_2(4a+2b)^2$ to a good approximation. Higher order sums simply involve higher powers of $(4a+2b)$. The cancellations needed for convergence come from the so-called ladder diagrams, which are important in calculating the t matrix of nuclear physics. Additional terms that help convergence come from the EPV diagrams of Sec. IIIC, but the effects of ladder diagrams are greater.

A third-order ladder diagram is shown in Fig. 9(b). The sign of the diagram is positive, and there are two energy denominators that are always negative. The contribution to the correlation energy is positive and tends to cancel E_2 . In all ladder diagrams considered it is assumed that all excited states have the same l unless it is explicitly stated otherwise. Scattering processes as in Fig. 9(b), where k and k' have one value of l and k'' and k''' have a different value of l , are considered later. Calculations of third-order ladder diagrams are lengthy since four integrations are involved. However, a simplification is achieved by assuming that the relative magnitudes of the different k and k' excitations remain unchanged under such an interaction. The effect of the ladder interaction is then to multiply the lower order diagram by a constant factor. This assumption is similar to that which led to Eq. (5.10), and it is justified by the numerical calculations. The third-order ladder term is written as $E_{3t}(l; 2s, 2s)$ and

$$t(l; 2s, 2s) = E_{3t}(l; 2s, 2s)/E_2(l; 2s, 2s). \quad (5.11)$$

To a good approximation,

$$t(l; 2s, 2s) = \left[\left(\frac{2}{\pi} \right)^2 \int_0^\infty dk \int_0^\infty dk' \langle k''k'''|l|v|kk'; l \rangle \frac{1}{D(k, k')} \times \langle kk'; l|v|2s2s \rangle \right] / \langle k''k'''|l|v|2s2s \rangle, \quad (5.12)$$

TABLE II. The effects of hole-particle EPV interactions on excited states.

k (atomic units)	k''	$a_{app}(1; 2s, 2s)/a(1; 2s, 2s)$
0.2	0.4	1.060
0.4	0.2	0.995
0.4	0.4	1.017
0.4	0.8	1.165 ^a
0.6	0.2	0.957
0.6	0.4	0.960

^a The most important contributions come from k, k'' between 0.2 and 0.6, with $k=k''=0.4$ most nearly in the center of the range of important excitations.

where the excited states all have orbital momentum, l , and the states k'' , k''' are chosen as typical excited states contributing to the diagram. Sums over m and m' , the azimuthal quantum numbers of k and k' , are implied in Eq. (5.12). By use of the assumption of Eq. (5.12), the ladder diagrams may be summed, including second order, to give $E_2(1-t)^{-1}$, where t is negative. When the reduction of energy terms caused by the third class of EPV diagrams, given by Eq. (3.16), is included, the ladder diagrams sum geometrically to

$$E_2(1-\gamma S)[1-t(1-\gamma S)]^{-1}. \quad (5.13)$$

The factor

$$t_r = [1-t(1-\gamma S)]^{-1} \quad (5.14)$$

is an effective reduction of the Coulomb interaction due to summing ladder diagrams. If a nonladder interaction is multiplied by t_r , the effect is a summation of all ladder terms of fixed l between it and the next higher non-

TABLE III. Calculations of ladder effects using different intermediate excitations.

k'' (atomic units)	k'''	$t(1; 2s, 2s)^a$	$t_r(1; 2s, 2s)^b$
0.4	0.4	-0.3620	0.7404
0.4	0.6	-0.3785	0.7317
0.4	0.8	-0.4120 ^c	0.7147

^a See Eq. (5.12).

^b See Eq. (5.14).

^c The most important contributions to diagrams are from $k=0.20$ to $k=0.60$.

ladder or l -changing ladder interaction. The total correlation energy among $2s$ electrons for intermediate states of fixed l is written

$$\begin{aligned} E_{\text{corr}}(l; 2s, 2s) &= E_2 t_r (1-\gamma S) [1 + (4a+2b)t_r(1-\gamma S) \\ &\quad + (4a+2b)^2 t_r^2 (1-\gamma S)^2 + \dots] = E_2 t_r (1-\gamma S) \\ &\quad \times [1 - (4a+2b)t_r(1-\gamma S)]^{-1}, \end{aligned} \quad (5.15)$$

where the arguments l and $2s, 2s$ are implied in the quantities on the right.

It is convenient to introduce still another symbol

$$\text{Ce}(l; 2s, 2s) = t_r(1-\gamma S) [1 - (4a+2b)t_r(1-\gamma S)]^{-1}. \quad (5.16)$$

The quantity $\text{Ce}(l; 2s, 2s)$ is now called the coefficient of enhancement and represents the factor by which a basic diagram is enhanced owing to repeated inter-

TABLE IV. Correlation energies among $2s$ electrons in Be for different l .^a

l	a	b	t	t_r	$\text{Ce}(l; 2s, 2s)$	$E_{\text{corr}}(l; 2s, 2s)$
0	0.18330	-0.02778	-0.1650	0.8622	1.925	-0.003704
1	0.28504	-0.06158	-0.3620	0.7404	2.652	-0.04256
2	0.16480	-0.01423	-0.2113	0.8301	1.632	-0.005321

^a All energies are in atomic units.

TABLE V. Contributions to the correlation energy among $2s$ electrons in Be.

Term ^a	Energy (a.u.)
$E_{\text{corr}}(0)$	-0.003704
$E_{\text{corr}}(1)$	-0.04256
$E_{\text{corr}}(2)$	-0.005321
$E_{3\text{Ce}}(0,1)$	0.00203
$E_{3\text{Ce}}(1,0)$	0.00203
$E_{3\text{Ce}}(1,2)$	0.00282
$E_{3\text{Ce}}(2,1)$	0.00282
$E_{4\text{Ce}}(0,1,0)$	-0.000096
$E_{4\text{Ce}}(0,1,2)$	-0.000107
$E_{4\text{Ce}}(1,0,1)$	-0.001109
$E_{4\text{Ce}}(1,2,1)$	-0.000959
$E_{4\text{Ce}}(2,1,0)$	-0.000107
$E_{4\text{Ce}}(2,1,2)$	-0.000120
$\sum_{n=5}^{\infty} E_{n\text{Ce}}$	0.00051
Total	-0.04387

^a The arguments $2s, 2s$ are implied.

actions in which the value of l remains unchanged. Reference to Eq. (5.15) and then to Eq. (3.14) for S shows that there is a problem of self-consistency. It is necessary to know S in order to calculate $E_{\text{corr}}(l; 2s, 2s)$, but S is determined from the sum of energy diagrams for all l values. By use of Eq. (3.10), γ was calculated as $-0.7887 \text{ a.u.}^{-1}$. In this calculation $S(2s, 2s) = -0.0395 \text{ a.u.}$; this value may be checked for consistency after calculation of all energy terms. Results of the numerical calculations of $t(1; 2s, 2s)$ and $t_r(1; 2s, 2s)$ are presented in Table III for different $k''=k'''$. The excitations $k''=k'''=0.40$ are expected to give the most accurate result of those listed because they are most nearly in the middle of the range of important excitations. By use of this result for t_r and the other numerical results already reported for $S, \gamma, (4a+2b)$, and E_2 , it was found from Eq. (5.15) that $E_{\text{corr}}(1; 2s, 2s) = -0.04256 \text{ a.u.}$ From Eq. (5.16), $\text{Ce}(1; 2s, 2s) = 2.6515$. If an average of the three t values of Table III is made, then $E_{\text{corr}}(1; 2s, 2s) = -0.0402 \text{ a.u.}$ and $\text{Ce}(1; 2s, 2s) = 2.5042$. The first calculation of $E_{\text{corr}}(1; 2s, 2s)$ is believed to be more accurate, but the second calculation gives some indication of the error. Results for the correlation energies among the $2s$ electrons are listed in Table IV for three values of l . Most of the correlation energy comes from $l=1$ contributions. The sum for $l=0, 1$, and 2 is -0.0516 a.u.

There are still more diagrams involving only $2s$ unexcited states. These are ladder diagrams in which the interaction changes the value of l for the excited states. The third-order energy diagram of this type is written $E_3(l, l'; 2s, 2s)$, where $l \neq l'$. The enhanced diagram

$$E_{3\text{Ce}}(l, l'; 2s, 2s) = E_3(l, l'; 2s, 2s) \text{Ce}(l; 2s, 2s) \times \text{Ce}(l'; 2s, 2s) \quad (5.17)$$

corresponds to the summation of all possible diagrams in which there is only one change of orbital angular

TABLE VI. Correlation energies among 1s electrons in Be for different l .^a

l	a	b	t	t_r	$Ce(l; 1s, 1s)$	$E_{corr}(l; 1s, 1s)$
0	0.07672	-0.01823	-0.08784	0.9193	1.222	-0.01408
1	0.07614	-0.01302	-0.10205	0.9075	1.213	-0.02518
2					1.20 ^b	-0.00414

^a Energies are in atomic units.^b This value was estimated.

momentum, from l to l' , in the excited states. The corresponding enhanced fourth-order energy diagram is $E_{4Ce}(l, l', l''; 2s, 2s)$, where $l \neq l' \neq l''$. As might be expected from the previous numerical results, the most important diagrams of this type are those in which $l = l'' = 1$. The approximation of Eq. (5.12) was used in calculating diagrams in which l changes. The results are listed in Table V along with previous calculations of E_{corr} from Table IV. The sum of all these terms is the total correlation energy among the 2s electrons of Be and is -0.0439 a.u. It is believed that all diagrams that can be of importance have been included in this calculation. It is interesting to note that the total calculated correlation energy among 2s electrons is very nearly that obtained from a consideration of $l=1$ terms alone. Correlations involving $l=0$ and $l=2$ states are very nearly cancelled by the ladder diagrams that involve changes from $l=1$ states.

D. Correlations among 1s Electrons

Correlations among the 1s electrons are considered now for $l=0, 1$, and 2 intermediate states. Equations (5.10) through (5.17) are used in the calculations with the arguments $2s, 2s$ replaced by $1s, 1s$. Results are listed in Table VI. The quantity γ in Eq. (3.10) equals -0.0286 a.u.⁻¹ and is much smaller than that for the 2s calculations because of the larger energy denominators for the 1s diagrams. In these calculations $S = -0.040$ a.u. The coefficient of enhancement $Ce(2; 1s, 1s)$ was estimated. As in the case of 2s correlations, there are terms in which the excited electrons change orbital momentum after the interactions. All calculated contributions to the 1s correlations are listed in Table VII. The terms $E_{3Ce}(l, l'; 1s, 1s)$ are less important for 1s than for 2s correlations.

TABLE VII. Contributions to the correlation energy among 1s electrons in Be.

Term ^a	Energy (a.u.)
$E_{corr}(0)$	-0.01408
$E_{corr}(1)$	-0.02518
$E_{corr}(2)$	-0.00414
$E_{3Ce}(1, 0)$	0.000412
$E_{3Ce}(0, 1)$	0.000412
$E_{3Ce}(1, 2)$	0.000226
$E_{3Ce}(2, 1)$	0.000226
Total	-0.04212

^a The arguments 1s, 1s are implied.

E. Correlations between 1s and 2s Electrons

The results of the second-order energy correlations among 1s and 2s electrons are listed in Table I, where the total 1s-2s correlation energy is -0.00497 a.u. The coefficients of enhancement $Ce(l; 1s, 2s)$ have not been calculated, but are expected to be small because the energy denominators are much larger than for the 2s calculations. A rough estimate for the coefficients of enhancement for the 1s-2s diagrams is 1.10 to 1.20. Third-order diagrams that tend to reduce the 1s-2s correlation energy are the ring diagrams, which were found to be of great importance in calculating the correlation energy of a dense electron gas.² A typical third-order ring diagram is shown in Fig. 10(a). This diagram was calculated and found to be 0.0000136 a.u. There are eight such diagrams, each of which should be multiplied by the appropriate coefficient of enhancement. The result is approximately 0.000288 a.u. There are additional diagrams in which the relative positions of the 1s and 2s states differ from those shown in Fig. 10(a). The approximate sum of all third-order ring diagrams, including enhancement, is 0.0007 a.u. The ring diagrams are reduced by the hole-particle diagrams of Fig. 10(b). These diagrams are quite small, like the ring diagrams. However, there are not so many hole-particle diagrams because spins must be parallel in scattering from one unexcited state to another. A very rough estimate indicates that these diagrams reduce the ring diagrams by one-third. It seems then that the combined effects of enhancement, ring diagrams, and hole-particle diagrams roughly cancel for 1s-2s correlations and that the second-order result may be used. It should be remembered, however, that certain higher order diagrams are included, since the second-order calculations were made with shifted energy denominators.

By use of the results of the 1s- and 2s-correlation energies, physical arguments may be used to estimate the 1s-2s correlation energy. Reference to the Be wave functions of Kibartas and Yutsis shows that the radial distribution for 1s electrons, P_{1s}^2 , is peaked sharply at $r=0.26$ a.u.¹⁷ The normalization of P_{1s} and P_{2s} is

$$\int_0^\infty P_{1s}^2 dr = \int_0^\infty P_{2s}^2 dr = 1. \quad (5.18)$$

The ratio P_{2s}^2/P_{1s}^2 represents the relative probability of finding a 2s electron. Neglecting exchange, the 1s-2s correlation energy should be given roughly by the product of P_{2s}^2/P_{1s}^2 and the total correlation energy for the 1s electrons. At $r=0.26$ a.u., $P_{2s}^2/P_{1s}^2 = 0.0259$, and the resulting 1s-2s correlation energy is -0.00109 a.u. Since there are four 1s-2s pairs, the energy becomes -0.00436 a.u. It is also necessary to consider the ratio P_{1s}^2/P_{2s}^2 , where P_{2s}^2 peaks. This is more difficult because P_{2s}^2 is not so sharply peaked as P_{1s}^2 , which is a rapidly decaying exponential in the region where P_{2s}^2

is large. At best, it may be estimated that the correlations due to P_{1s}^2 contributions, where P_{2s}^2 is large, are a little smaller than those due to P_{2s}^2 contributions, where P_{1s}^2 peaks. Since the exchange contributions may be expected to be somewhat less than half the total $1s-2s$ correlation energy, the exchange energy should approximately cancel the contributions from considerations of large P_{2s}^2 . The result of these rough physical considerations is then -0.00436 a.u., which is in reasonable agreement with the result -0.00497 a.u. calculated from perturbation theory.

F. Discussion of Results

The sum of all correlation energies in Be, obtained from Tables V and VII and Sec. V E, is -0.09096 a.u. It is difficult to assess the accuracy of the calculations, but limits of ± 0.004 a.u. seem reasonable. In these calculations intermediate states were restricted to orbital angular momenta $l=0, 1$, and 2 . Additional contributions to the correlation energy may come from higher angular-momentum states, and these will probably affect the $1s$ more than the $2s$ -correlation results. The result for the total correlation energy compares favorably with the experimental value -0.0953 a.u., which was obtained from spectroscopic data¹² and Pekeris' energy for Be^{++} .¹⁵ Watson's calculation of the Be correlation energy by configuration interactions resulted in -0.0844 a.u. when he used thirty-seven configurations.¹⁴ However, he was able to obtain 74% of the correlation energy by use of only four configurations. Watson also found that about 5% of the correlation energy was caused by interactions between the $1s$ and $2s$ shells. This result also agrees favorably with the calculations of Sec. V E that gave -0.004966 a.u. for the $1s-2s$ correlation energy. It is interesting to note that correlations among $1s$ and $2s$ electrons, though small, must be considered if accurate values for the correlation energy are desired. The fact that four such pairs must be considered increases their effect.

The calculations reported here may also be compared with those of Linderberg and Shull.²⁰ For $Z=4$ in the He-like series, they find by use of configuration interaction that the total correlation energy is -0.0439 a.u. and that $l=1$ terms contribute -0.0217 a.u. and $l=2$ terms contribute -0.0025 a.u. The corresponding results of Table VII agree reasonably well with these figures. Linderberg and Shull also report that in Be, the $2s$ correlations are almost entirely due to $l=1$ contributions that give -0.043 a.u. This value agrees with the results of Table V when the l -changing ladder-diagram results are included.

VI. APPROXIMATE METHODS FOR CORRELATION ENERGIES

At the beginning of this investigation the correlation energy of boron was calculated by use of second-order

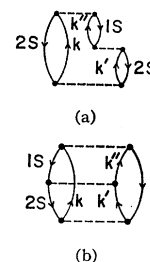


FIG. 10. (a) A typical ring diagram. (b) A hole-particle diagram.

perturbation theory.²¹ In order to simplify the numerical work, the Hartree-Fock potential was approximated by the screened Coulomb potential in which the excited states were calculated. The bound states were solutions of the Hartree-Fock equations. The results for the correlations among the $1s$ electrons were in good agreement with the energies reported by Linderberg and Shull.²⁰ However, the correlations among the $2s$ electrons were much too large. The poor results for the $2s$ correlations may be attributed to the fact that the important excited states for $2s$ matrix elements are those of low energy ($k \sim 0.3$ a.u.), whereas the important excitations for $1s$ matrix elements are in the range $k \sim 4.0$ a.u. On physical grounds, it is expected that wave functions for high energies will not be affected by the details of the potential so much as will low-energy wave functions. Since the approximate solutions are not orthogonal to the ground state HF wave functions, it is not surprising that the matrix elements are too large. These results indicate the importance of using the correct Hartree-Fock excited states in the perturbation theory.

An estimate of the total correlation energy as a function of the atomic number Z was obtained from the Gell-Mann and Brueckner² formula for the correlation energy of a dense electron gas:

$$\epsilon_c = -0.096 + 0.0622 \ln r_s \text{ Ry per particle.} \quad (6.1)$$

The dimensionless spacing parameter r_s depends upon the particle density. Assuming that the density of electrons, ρ , within the atom is given by a Fermi-Thomas distribution,²² the resulting total correlation energy is

$$E_{\text{corr}} = \int \epsilon_c(\rho) \rho d\tau = -Z[0.0062 + 0.0207 \ln Z] \text{ a.u.} \quad (6.2)$$

This formula gives a rough estimate of E_{corr} and is too large by a factor of approximately 2 for small Z . The Fermi-Thomas electron distribution fulfills the requirements of a dense electron gas only for the inner part of the atom for low Z .

²¹ H. Kelly, in *Proceedings of the Second International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers* (W. A. Benjamin, Inc., New York, 1961), p. 136.

²² E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 335.

VII. CONCLUSIONS

By use of Hartree-Fock wave functions, accurate perturbation-theory calculations were made of the correlation energies among the electrons of Be. The total calculated correlation energy was found to be -0.0910 a.u. as compared with -0.0953 a.u., which is believed to be the correct result. The correlations in the $1s$ and $2s$ shells were found to be each approximately one-half of the total, and the intershell correlations contributed approximately 6% of the total correlation energy. In calculating the $2s$ correlations it was found that the exclusion-principle-violating (EPV) diagrams are extremely important and that these must be summed to high orders. It is expected that EPV diagrams will be important in calculating outer electron correlations in all atoms. If accurate results are desired, it is necessary to include the intershell correlations. These may become more important as the atomic number increases beyond four because the $2s$ and $2p$ wave functions are expected to overlap more than $1s$ and $2s$ wave functions. When the number of $2p$ electrons equals three or more, it is possible to have third-order ring diagrams in which all three unexcited-state wave functions are the same, and the higher-order ring diagrams may be more important for such atoms than for those of fewer electrons. The third-order ring diagrams in Be were found to be very small. The calculations on boron indicate the importance of using Hartree-Fock wave functions for the excited states.

It has been shown in this investigation that many-body perturbation theory is very useful in correcting atomic energies. Although the complexity of the calculation increases with the number of electrons, this method should still be quite useful in calculating correlations in many-electron atoms. When there are open shells, the calculation may be less accurate because of the lack of spherical symmetry in the true atomic potentials. There may also be the difficulty due to the necessity of distinguishing between single-particle states with different spins. This theory is also applicable in obtaining correlation corrections for atomic wave

functions and therefore for all atomic properties. Future investigations will examine the correlation corrections for transition probabilities and nuclear quadrupole coupling constants.

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APPENDIX

In Sec. III C formulas were given to account for the effects of the third class of EPV diagrams. These diagrams arise from factorizations in which the unlinked part is of second order or higher. It was shown that L_1 is modified by the factor $(1-\gamma E_2)$. In a similar way it may be shown that, to a good approximation, the linked diagram L_m is modified by $(1-\gamma S)^m$, where S is given by Eq. (3.14). Since these formulas are concerned with correlations between two electrons, each diagram has the same unexcited states, although there is no limit to the number of hole lines. Other cases may be handled similarly.

Consider the diagrams of Fig. 11. The results must be the same for any unlinked third-order diagram. After factorization, three EPV diagrams remain and sum to $-\gamma L_1(p,q)E_{3i}(p,q)$ in the approximation of Eq. (3.9). The fraction under each diagram gives the fraction of $-\gamma L_1 E_{3i}$ and is determined from the increased energy denominators. A consideration of higher order unlinked diagrams with L_1 shows that the reduction is still the same and so $L_1(p,q)$ is modified by $[1-\gamma \sum_{m=2}^{\infty} E_m(p,q)]$. If factorizations like that of Fig. 11 are made with a linked part $L_2(p,q)$ and an unlinked

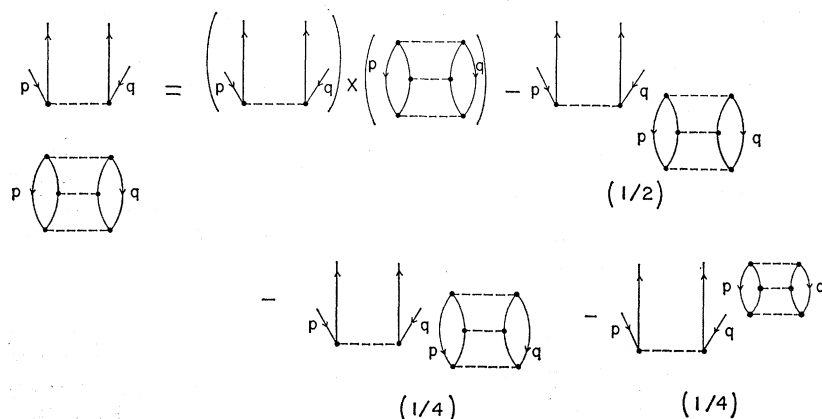


FIG. 11. Factorization of $L_1(p,q)$ and $E_{3i}(p,q)$. The three subtracted diagrams on the right are EPV diagrams that sum to $-\gamma L_1(p,q)E_{3i}(p,q)$ in the approximation of Eq. (3.9). Fractions of this sum are shown below each diagram. The arrows and labels are implied for excited states when not written explicitly.

part of second order or higher, the result is that $L_2(p, q)$ is modified by $[1 - 2\gamma \sum_{m=2}^{\infty} E_m(p, q)]$. The general result is that the linked diagram $L_n(p, q)$ is multiplied by the factor $[1 - n\gamma \sum_{m=2}^{\infty} E_m(p, q)]$, and this may be verified by an examination of higher order linked diagrams. The form $[1 - \gamma \sum_{m=2}^{\infty} E_m(p, q)]^n$ is now suggested as the modification of $L_n(p, q)$, and this form may be checked as approximately correct by enumeration of the EPV diagrams resulting from factorizations of diagrams like Fig. 12.

Before the factorizations of Fig. 12 are actually made, the factorizations of Fig. 13 should be investigated. These lead to further modifications of the factor $[1 - \gamma \sum_{m=2}^{\infty} E_m(p, q)]^n$ for $L_n(p, q)$. After the factorizations of Fig. 13, there are three factored diagrams $G0$, $G1F$, and $G2F$ and a sum of EPV diagrams that add to $L_1 3(\gamma E_2)^2$. The diagram L_1 is now modified to

$$L_1[1 - \gamma E_2(1 - 3\gamma E_2)]. \quad (A1)$$

The form

$$L_1[1 - \gamma E_2(1 - \gamma E_2)^3] \quad (A2)$$

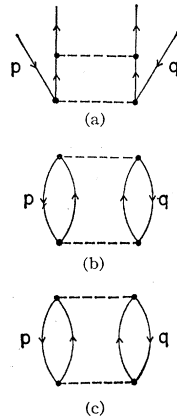
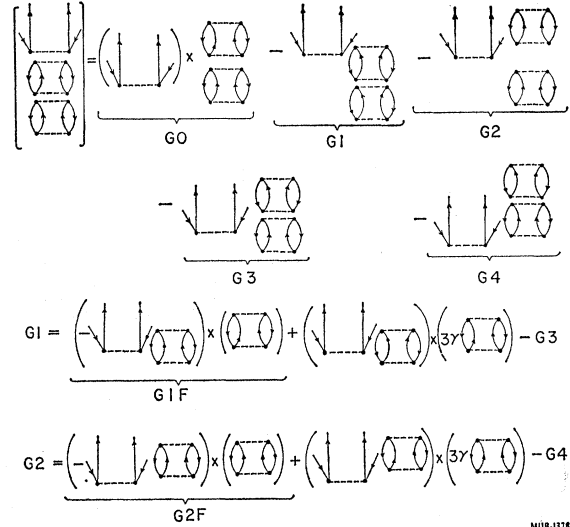


FIG. 12. Factorization of this diagram leads to the modification of $L_2(p, q)$ given by Eq. (A3).



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FIG. 13. EPV diagrams resulting from factorization of the diagram shown at the top left. After all factorizations there are three factored diagrams $G0$, $G1F$, and $G2F$ and a sum of EPV diagrams that add to modify L_1 to $L_1[1 - \gamma E_2(1 - 3\gamma E_2)]$. The hole line on the left of each disconnected part refers to the state ϕ_p and the hole line on the right refers to the state ϕ_q .

is then suggested and may be checked. Further factorizations of diagrams like Fig. 12 indicate that a good approximation to the modifications is given by

$$L_n(p, q)(1 - \gamma S)^n, \quad (A3)$$

where

$$S(p, q) = \sum_{m=2}^{\infty} E_m(p, q)[1 - \gamma S(p, q)]^{m+1}. \quad (A4)$$

Factorizations of L_1 and three unlinked parts indicate that S on the right of Eq. (A4) should be modified approximately by $(1 - \gamma S)^2$. This last modification leads to Eq. (3.14). The modifications for the energy diagrams are readily obtained from (A3), since E_m is related to L_{m-1} . The validity of considering all hole-hole EPV diagrams summed in making this analysis may be checked by a consideration of the appropriate factorizations.