

Many-body perturbation-theory formulas for energy levels of excited states of closed-shell atoms

E. Avgoustoglou, W. R. Johnson, D. R. Plante, J. Sapirstein, and S. Sheinerman

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

S. A. Blundell*

University of California, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550

(Received 4 May 1992)

Many-body perturbation-theory formulas are derived for one-particle-one-hole excited states of closed-shell atoms. Both analytic results and Goldstone diagrams complete through third order are presented, and a sample calculation of a transition energy in neonlike xenon is carried out.

PACS number(s): 31.10.+z, 31.20.Di, 31.20.Tz, 31.30.Jv

I. INTRODUCTION

Many-body perturbation theory (MBPT) provides a systematic method for the calculation of atomic properties. However, the complexity of each order of MBPT increases rapidly, and complete calculations beyond third order in atomic physics have rarely been carried out. It is also possible to sum infinite classes of MBPT diagrams using various "all-orders" methods [1]. These methods, except for very light atoms, are always incomplete, since not all diagrams of a given order are in general included by the methods. It is of interest to evaluate MBPT through the highest possible order for two reasons. The first is that such a procedure provides a guide for all-orders methods. If such a method misses diagrams that can be explicitly shown to be large, it must be modified to include them. A second reason is that MBPT converges quickly for some systems, particularly highly charged ions. In a series of works [2] on the lithium, sodium, and copper isoelectronic sequences, it has been shown that evaluation of MBPT through third order provides highly convergent results for the spectra of these ions. It is the purpose of this paper to generalize the formulas derived for atoms or ions with one electron outside a closed shell [3] to excited states of closed-shell atoms or ions. Specifically, we concentrate on *particle-hole* excitations, in which an electron is removed from one of the closed shells, creating a hole, and excited into a valence orbital, creating a particle. Such states have a richer spectrum than the alkali metals previously considered, and the formulas are correspondingly more complex. For this reason we consider it of value to set these formulas down analytically through third order along with their graphical representation in terms of Goldstone diagrams. We will in a later work present explicit calculations of a number of isoelectronic sequences using these results.

The plan of the paper is as follows. Section II reviews the second-quantized form of Rayleigh-Schrödinger perturbation theory. In Sec. III the first- and second-order formulas are presented. Section IV contains the relatively lengthy formulas for the third-order energy, and Sec. V contains a discussion of how the formulas can be numeri-

cally evaluated along with a sample application to neonlike xenon. Finally, angular reductions of the formulas are given in an appendix.

II. FORMALISM

For most atoms, an exact solution to the Schrödinger or Dirac equation is not attainable because of the complexity of the interactions between the electrons. However, a reasonable lowest-order approximation can frequently be found in which each electron is assumed to move independently in a central potential $U(r)$ that mocks up the effect of the other electrons. The actual interactions can then be accounted for in perturbation theory by setting $H = H_0 + V$, where

$$H_0 = \sum_{i=1}^N h(\mathbf{r}_i) + \sum_{i=1}^N U(r_i), \quad (1)$$

$$V = - \sum_{i=1}^N U(r_i) + \sum_{i < j}^N \frac{e^2}{r_{ij}}, \quad (2)$$

where for the nonrelativistic case

$$h(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{nuc}}(r) \quad (3)$$

and for the relativistic case

$$h(\mathbf{r}) = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_{\text{nuc}}(r). \quad (4)$$

The form of the potential is left arbitrary at this point. It should be noted that the many-electron Dirac equation has meaning only within the framework of field theory, which provides a consistent set of rules for the treatment of negative energy states. For most atomic structure calculations it suffices to simply exclude negative energy states when summing over a complete set of intermediate states, as the excluded terms are radiative corrections that are generally quite small.

It is now straightforward to solve $H_0\psi_0 = E_0\psi_0$ in terms of a Slater determinant formed from single-electron

orbitals $u_i(\mathbf{r})$ with energies ε_i obeying

$$[h(\mathbf{r}) + U(r)]u_i(\mathbf{r}) = \varepsilon_i u_i(\mathbf{r}). \quad (5)$$

H_0 and V can now be written in second-quantized form as

$$H_0 = \sum_i \varepsilon_i a_i^\dagger a_i, \quad (6)$$

$$V = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum_{i,j} U_{ij} a_i^\dagger a_j, \quad (7)$$

where g_{ijkl} are Coulomb matrix elements defined by

$$g_{ijkl} = \alpha \int \frac{d^3 r d^3 r'}{|\mathbf{r} - \mathbf{r}'|} u_i^\dagger(\mathbf{r}) u_j^\dagger(\mathbf{r}') u_k(\mathbf{r}) u_l(\mathbf{r}'), \quad (8)$$

and U_{ij} are the matrix elements of the model potential,

$$U_{ij} = \int d^3 r u_i^\dagger(\mathbf{r}) U(r) u_j(\mathbf{r}). \quad (9)$$

The Hartree-Fock potential is defined in terms of the Coulomb matrix elements via

$$(V_{\text{HF}})_{ij} = \sum_c \tilde{g}_{icjc}, \quad (10)$$

where $\tilde{g}_{ijkl} = g_{ijkl} - g_{ijlk}$ and the sum over c is taken to run over the filled core orbitals of the ground state of a closed-shell system. As we are interested here in particle-hole excitations, we adopt the convention that sums over c, d, e, f will be only over core orbitals (including the hole orbital), sums over m, n, r, s will be only over excited orbitals (including the particle orbital), and sums over i, j, k, l will be over all orbitals. The letters a and b will be used to designate hole orbitals while the letters v and w will designate particle orbitals.

Using the definition of the Hartree-Fock potential, we now rewrite Eq. (7) using normal ordering as

$$V = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : + \sum_{i,j} V_{ij} : a_i^\dagger a_j : + V_0, \quad (11)$$

where

$$V_{ij} = (V_{\text{HF}} - U)_{ij}, \quad (12)$$

and

$$V_0 = \sum_d \left(\frac{1}{2} V_{\text{HF}} - U \right)_{dd}. \quad (13)$$

We create a zeroth-order particle-hole wave function with total angular momentum JM via

$$|0_{\text{ph}}\rangle = F_{av} a_v^\dagger a_a |0_C\rangle, \quad (14)$$

where

$$F_{av} = \sum_{m_a, m_v} (-1)^{j_a - m_a} \langle j_v m_v, j_a - m_a | JM \rangle. \quad (15)$$

Here $|0_C\rangle$ is the closed-shell wave function and we adopt

a shorthand that a_a stands for $a_{n_a \kappa_a m_a}$ where n_a , κ_a , and m_a are the principal, angular momentum, and magnetic quantum numbers, respectively, of the core orbital that is being excited, and similarly for a_v^\dagger . The phase factor in the definition of this wave function is required to make a_a transform properly under rotations, and the factor $-m_a$ in the Clebsch-Gordan coefficient accounts for the fact that this is a hole state. We assume throughout that there is no mixing of states, so j_a and j_v are unique. We define the complex-conjugate wave function as

$$\langle 0_{\text{ph}} | = F_{bw} \langle 0_C | a_b^\dagger a_w, \quad (16)$$

where

$$F_{bw} = \sum_{m_b, m_w} (-1)^{j_a - m_b} \langle JM | j_v m_w, j_a - m_b \rangle, \quad (17)$$

with a_b^\dagger now standing for $a_{n_a \kappa_a m_b}^\dagger$ and similarly for a_w . Note that

$$F_{av} F_{bw} \delta_{ab} \delta_{vw} = 1. \quad (18)$$

Applying H_0 to Eq. (14) then gives

$$E^{(0)} = E_0 + \varepsilon_v - \varepsilon_a, \quad (19)$$

where

$$E_0 = \sum_c \varepsilon_c. \quad (20)$$

III. FIRST- AND SECOND-ORDER ENERGIES

Before proceeding, we observe that in deriving higher-order corrections to the energy, there are two methods which may be used. The first method is the direct algebraic manipulation of creation and annihilation operators. The second method is that of diagrammatic techniques. In the latter method, the results of perturbation theory are represented by Goldstone diagrams. It is particularly valuable because it allows the rapid generation of MBPT expressions through a set of straightforward rules. In general, the advantage of the algebraic approach is that it is extremely straightforward, being essentially a direct application of Wick's theorem. This is associated, however, with the disadvantage of a great deal of algebra. The advantage of the diagrammatic approach is the fact that an analytic formula can be obtained from a diagram quite easily, and also that structures in perturbation theory can sometimes be grasped in a very intuitive way, as with the identification of the random-phase approximation with ring diagrams. A disadvantage of the approach is that it is possible to miss diagrams with complicated topology, and also that the rules for symmetry factors require some experience to apply in high order. Because of the complexity of the results obtained in this paper, we have used both methods in obtaining the results in order to eliminate possible errors. Two independent algebraic results were cross-checked and found to agree with each other and a separate diagrammatic calculation.

We now choose the Hartree-Fock potential as the model potential. The perturbing potential then simplifies

to

$$V = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : - \frac{1}{2} \sum_{c,d} \tilde{g}_{cdcd}. \quad (21)$$

While there are good theoretical reasons that favor the use of this potential, its use is almost forced for the treatment through third-order MBPT of particle-hole states. This is simply because of the extremely large number of terms in third order; we would more than double the already very lengthy expression for the third-order energy given in Sec. IV without this simplification.

To determine the first-order energy, we need to solve

$$E^{(1)} = \langle 0_{\text{ph}} | V | 0_{\text{ph}} \rangle. \quad (22)$$

It is straightforward to show that

$$E^{(1)} = F_{av} F_{bw} (\delta_{ab} \delta_{vw} E_{\text{core}}^{(1)} + E_{av}^{(1)}), \quad (23)$$

where

$$|1_{\text{ph}} \rangle = F_{av} \left(\frac{1}{2} \sum_{m,n,c,d} \frac{g_{mncd}}{\varepsilon_{cd} - \varepsilon_{mn}} a_v^\dagger a_m^\dagger a_n^\dagger a_c a_d + \sum_{m,n,c} \frac{g_{mnvc}}{\varepsilon_{cv} - \varepsilon_{mn}} a_m^\dagger a_n^\dagger a_a a_c \right. \\ \left. + \sum_{m,c,d} \frac{g_{amcd}}{\varepsilon_{cd} - \varepsilon_{ma}} a_m^\dagger a_v^\dagger a_c a_d + \sum_{m,c} \frac{\tilde{g}_{mavc}}{\varepsilon_{vc} - \varepsilon_{ma}} a_m^\dagger a_c \right) |0_{\text{ph}} \rangle, \quad (28)$$

where $\varepsilon_{ij} \equiv \varepsilon_i + \varepsilon_j$, and the prime on the summation above implies that the sum is over all values for which the energy denominator is nonzero. In the above case, this means all m and c are summed over except when $m = v$ and $c = a$ concurrently. Inserting Eq. (28) into Eq. (26), we find

$$E^{(2)} = F_{av} F_{bw} (\delta_{ab} \delta_{vw} E_{\text{core}}^{(2)} + \delta_{ab} E_v^{(2)} + \delta_{vw} E_a^{(2)} + E_{av}^{(2)}), \quad (29)$$

where

$$E_{\text{core}}^{(2)} = \frac{1}{2} \sum_{m,n,c,d} \frac{g_{cdmn} \tilde{g}_{mncd}}{\varepsilon_{cd} - \varepsilon_{mn}}, \quad (30a)$$

$$E_v^{(2)} = \sum_{m,n,c} \frac{g_{wcmn} \tilde{g}_{mnvc}}{\varepsilon_{vc} - \varepsilon_{mn}} - \sum_{m,c,d} \frac{g_{cdmv} \tilde{g}_{mwcd}}{\varepsilon_{cd} - \varepsilon_{vm}}, \quad (30b)$$

$$E_a^{(2)} = - \sum_{m,n,c} \frac{g_{acmn} \tilde{g}_{mnbc}}{\varepsilon_{ac} - \varepsilon_{mn}} + \sum_{m,c,d} \frac{g_{cdmb} \tilde{g}_{macd}}{\varepsilon_{cd} - \varepsilon_{ma}}, \quad (30c)$$

$$E_{av}^{(2)} = Z^{(2)} + S_1^{(2)} + S_2^{(2)} + S_3^{(2)} + S_4^{(2)} + D^{(2)}. \quad (30d)$$

Here

$$Z^{(2)} = - \sum_{c,d} \frac{g_{cdbv} \tilde{g}_{awcd}}{\varepsilon_{cd} - \varepsilon_{va}}, \quad (31)$$

$$S_1^{(2)} = \sum_{m,c} \frac{\tilde{g}_{camv} \tilde{g}_{wmbc}}{\varepsilon_{ac} - \varepsilon_{vm}}, \quad (32)$$

$$S_2^{(2)} = \sum_{m,c} \frac{\tilde{g}_{wcbm} \tilde{g}_{amvc}}{\varepsilon_{vc} - \varepsilon_{ma}}, \quad (33)$$

$$E_{\text{core}}^{(1)} = - \frac{1}{2} \sum_{c,d} \tilde{g}_{cdcd}, \quad (24)$$

and

$$E_{av}^{(1)} = \tilde{g}_{awvb}. \quad (25)$$

While the first-order energy is simple to solve for, the second-order energy, while still straightforward, requires considerably more algebra. It can be expressed in terms of the first-order correction to the wave function $|1_{\text{ph}} \rangle$ as

$$E^{(2)} = \langle 0_{\text{ph}} | V | 1_{\text{ph}} \rangle, \quad (26)$$

where $|1_{\text{ph}} \rangle$ is obtained from

$$|1_{\text{ph}} \rangle = (H_0 - E^{(0)})^{-1} (E^{(1)} - V) |0_{\text{ph}} \rangle. \quad (27)$$

A short calculation gives

$$S_3^{(2)} = - \sum_{m,c} \frac{\tilde{g}_{wcv} \tilde{g}_{ambc}}{\varepsilon_c - \varepsilon_m}, \quad (34)$$

$$S_4^{(2)} = - \sum_{m,c} \frac{\tilde{g}_{camb} \tilde{g}_{wmvc}}{\varepsilon_c - \varepsilon_m}, \quad (35)$$

and

$$D^{(2)} = - \sum_{m,n} \frac{g_{wamn} \tilde{g}_{mnvb}}{\varepsilon_{va} - \varepsilon_{mn}}. \quad (36)$$

At this order the general structure of MBPT for particle-hole excitations can be discussed. Firstly, the terms labeled E_{core} give the energy of the ground state. They are always accompanied by the factors δ_{ab} and δ_{vw} that express the fact that the particle and hole states are unaffected. This term drops out in any transition energy. Secondly, the terms labeled E_v are related to the energy shift of a valence electron above a closed shell. They are always accompanied with a factor δ_{ab} , since the core electron is left unaffected. If one averages over the M values and uses

$$\frac{1}{2J+1} \sum_M F_{av} F_{bw} \delta_{ab} = 1 \quad (37)$$

it can be seen that these terms are identical to those given in Ref. [3]. Thirdly, the terms labeled E_a are closely related to the E_v terms, with the roles of v and a interchanged and the addition of an overall minus sign. This is a great advantage in the actual calculation, since the same code can be used to evaluate both terms. Finally, the E_{av} terms involve both the core and valence elec-

tron. We divide these terms into classes according to the number of excited-state summations present, using the notation Z for zero excited states, S for single, D for double, T for triple, and Q for quadruple excitations, with the latter two classes entering first in third order.

We now discuss the diagrammatic approach to the second-order energy. There are a total of 30 Goldstone diagrams in this order which are presented in Fig. 1. The upgoing line with a double arrow represents the state v when entering the diagram and w when leaving it. The downgoing line with a double arrow represents the state a when leaving the diagram and b when entering it. The usual Goldstone rules apply but must be supplemented with the following additional rule. This is that an extra factor of -1 is to be multiplied whenever the v line connects to the w line, which occurs in conjunction of course with the a line connecting to the b line. Thus, for example, the fourth diagram in S_1 , which has no loops and one core line, would normally enter with a negative sign, but the new rule makes the overall sign positive.

While 30 diagrams are shown in Fig. 1, there are only 11 analytic expressions in Eq. (30), which follows from the use of antisymmetrized Coulomb matrix elements in those expressions. Because of the very large number of terms in third order, we will in the following only show the "direct" diagram with all $\tilde{g}_{ijkl} \rightarrow g_{ijkl}$. Another simplification we will make use of is the fact that some terms in MBPT are complex conjugates of each other, which since the energy is real allows only one of them to be calculated provided the result is doubled. In second order this occurs with $S_3^{(2)}$ and $S_4^{(2)}$. The diagrams are related by a reflection through a horizontal axis, and the complex

conjugate of $S_3^{(2)}$ can be shown to be equal to $S_4^{(2)}$ when multiplied by $F_{av}F_{bw}$ and interchanging dummy indices. For this reason, we will in the following explicitly show only one of the pair of related terms, writing "+c.c." to indicate the other term, and likewise we will show only one of the pairs of related diagrams.

IV. THIRD-ORDER ENERGIES

We now turn to the calculation of the third-order energy. It can be expressed as

$$E^{(3)} = \langle 0_{\text{ph}} | V | 2_{\text{ph}} \rangle, \quad (38)$$

or

$$E^{(3)} = \langle 1_{\text{ph}} | V | 1_{\text{ph}} \rangle - E^{(1)} \langle 1_{\text{ph}} | 1_{\text{ph}} \rangle. \quad (39)$$

We proceed by using Eq. (28) in Eq. (39). Separating out the constant term in V from Eq. (21) allows us to write

$$E^{(3)} = E_{1V1}^{(3)} + E_{\text{fold}}^{(3)}, \quad (40)$$

where

$$E_{1V1}^{(3)} = \langle 1_{\text{ph}} | (V - E_{\text{core}}^{(1)}) | 1_{\text{ph}} \rangle \quad (41)$$

and

$$E_{\text{fold}}^{(3)} = -(E^{(1)} - E_{\text{core}}^{(1)}) \langle 1_{\text{ph}} | 1_{\text{ph}} \rangle. \quad (42)$$

The subscript "fold" in Eq. (42) refers to the fact that these terms are represented by "folded" diagrams [4] as will be described in more detail later. The evaluation of $E_{1V1}^{(3)}$ requires a very lengthy algebraic manipulation. We

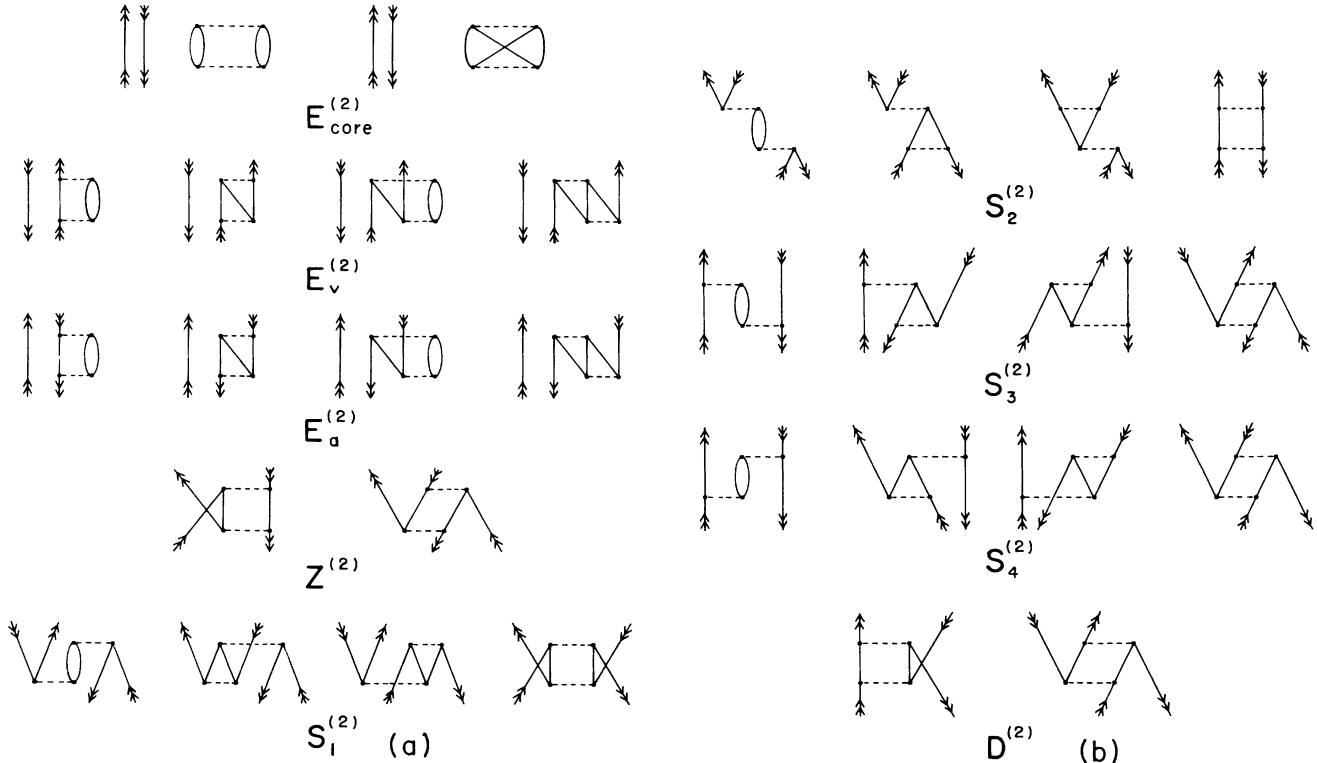


FIG. 1. Goldstone diagrams representing the second-order energy given in Eq. (30).

express the solution as follows:

$$E_{1V1}^{(3)} = F_{av}F_{bv}(\delta_{ab}\delta_{vv}E_{\text{core}}^{(3)} + \delta_{ab}E_v^{(3)} + \delta_{vw}E_a^{(3)} + E_{av}^{(3)}), \quad (43)$$

where $E_{\text{core}}^{(3)}$, $E_v^{(3)}$, $E_a^{(3)}$, and $E_{av}^{(3)}$ are the third-order generalizations of the structures encountered in second order. Because the expressions for $E_{\text{core}}^{(3)}$, $E_v^{(3)}$, and $E_a^{(3)}$ and their associated Goldstone diagrams have been treated in detail in Refs. [1] and [5] we do not discuss them further here. We note only that, as with the second-order energy, $E_{\text{core}}^{(3)}$ can be dropped in calculations of transition energies, and that the calculation of $E_a^{(3)}$ is carried out in exactly the same fashion as $E_v^{(3)}$ with the replacement of v with a and inclusion of an overall minus sign. The $E_{av}^{(3)}$ terms break into five classes, with 1 zero-excitation term, 11 single-excitation terms, 26 double-excitation terms, 11 triple-excitation terms, and 1 quadruple-excitation term,

$$E_{av}^{(3)} = F_{av}F_{bv}(E_Z^{(3)} + E_S^{(3)} + E_D^{(3)} + E_T^{(3)} + E_Q^{(3)}). \quad (44)$$

The second term in Eq. (40) breaks into nine terms,

$$E_{\text{fold}}^{(3)} = -(E^{(1)} - E_{\text{core}}^{(1)}) F_{av}F_{bv} \sum_{i=1}^9 F_i. \quad (45)$$

The zero-excited state term is given by

$$Z^{(3)} = - \sum_{c,d,e,f} \frac{\tilde{g}_{efvb}g_{cdef}g_{wacd}}{(\epsilon_{cd} - \epsilon_{av})(\epsilon_{ef} - \epsilon_{av})}. \quad (46)$$

The single-excited state terms are

$$S_1^{(3)} = - \sum_{m,c,d,e} \frac{\tilde{g}_{ecvm}\tilde{g}_{adbe}\tilde{g}_{mwcd}}{(\epsilon_{cd} - \epsilon_{vm})(\epsilon_{ce} - \epsilon_{vm})}, \quad (47a)$$

$$S_2^{(3)} = \sum_{m,c,d,e} \frac{\tilde{g}_{cemb}\tilde{g}_{dwve}\tilde{g}_{macd}}{(\epsilon_{cd} - \epsilon_{am})(\epsilon_{ce} - \epsilon_{am})}, \quad (47b)$$

$$S_3^{(3)} = \sum_{m,c,d,e} \frac{g_{demv}\tilde{g}_{cade}\tilde{g}_{wmbc}}{(\epsilon_{ac} - \epsilon_{vm})(\epsilon_{de} - \epsilon_{vm})} + \text{c.c.}, \quad (47c)$$

$$S_4^{(3)} = \sum_{m,c,d,e} \frac{\tilde{g}_{cemv}\tilde{g}_{dweb}\tilde{g}_{macd}}{(\epsilon_{ce} - \epsilon_{vm})(\epsilon_{cd} - \epsilon_{am})} + \text{c.c.}, \quad (47d)$$

$$S_5^{(3)} = - \sum_{m,c,d,e} \frac{\tilde{g}_{ecmv}g_{dwec}\tilde{g}_{madb}}{(\epsilon_{ce} - \epsilon_{vm})(\epsilon_d - \epsilon_m)} + \text{c.c.}, \quad (47e)$$

$$S_6^{(3)} = - \sum_{m,c,d,e} \frac{\tilde{g}_{cevm}\tilde{g}_{mdeb}\tilde{g}_{wacd}}{(\epsilon_{ce} - \epsilon_{vm})(\epsilon_{cd} - \epsilon_{av})} + \text{c.c.}, \quad (47f)$$

$$S_7^{(3)} = - \sum_{m,c,d,e} \frac{\tilde{g}_{ecvm}g_{mdce}\tilde{g}_{awbd}}{(\epsilon_{ce} - \epsilon_{vm})(\epsilon_d - \epsilon_v)} + \text{c.c.}, \quad (47g)$$

$$S_8^{(3)} = \sum_{m,c,d,e} \frac{\tilde{g}_{ecmb}\tilde{g}_{dmve}\tilde{g}_{wacd}}{(\epsilon_{cd} - \epsilon_{av})(\epsilon_{ce} - \epsilon_{am})} + \text{c.c.}, \quad (47h)$$

$$S_9^{(3)} = - \sum_{m,c,d,e} \frac{\tilde{g}_{demv}\tilde{g}_{cade}\tilde{g}_{wmbc}}{(\epsilon_{de} - \epsilon_{am})(\epsilon_c - \epsilon_m)} + \text{c.c.}, \quad (47i)$$

$$S_{10}^{(3)} = \sum_{m,c,d,e}' \frac{\tilde{g}_{wemb}g_{cdve}\tilde{g}_{macd}}{(\epsilon_{cd} - \epsilon_{am})(\epsilon_{ve} - \epsilon_{am})} + \text{c.c.}, \quad (47j)$$

$$S_{11}^{(3)} = - \sum_{m,c,d,e}' \frac{\tilde{g}_{wevb}g_{cdme}\tilde{g}_{amdc}}{(\epsilon_{cd} - \epsilon_{am})(\epsilon_e - \epsilon_a)} + \text{c.c.} \quad (47k)$$

The double-excited state terms are

$$D_1^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{damn}\tilde{g}_{wcvd}g_{mncb}}{(\epsilon_{ac} - \epsilon_{mn})(\epsilon_{ad} - \epsilon_{mn})}, \quad (48a)$$

$$D_2^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{cdvm}\tilde{g}_{ambn}g_{wncd}}{(\epsilon_{cd} - \epsilon_{vn})(\epsilon_{cd} - \epsilon_{vm})}, \quad (48b)$$

$$D_3^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{advn}\tilde{g}_{cmnd}\tilde{g}_{wnbc}}{(\epsilon_{ad} - \epsilon_{vm})(\epsilon_{ac} - \epsilon_{vn})}, \quad (48c)$$

$$D_4^{(3)} = \sum_{m,c,d}' \frac{\tilde{g}_{dwbn}\tilde{g}_{cnmd}\tilde{g}_{macv}}{(\epsilon_{vc} - \epsilon_{am})(\epsilon_{vd} - \epsilon_{an})}, \quad (48d)$$

$$D_5^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{cdnb}\tilde{g}_{wnvm}g_{macd}}{(\epsilon_{cd} - \epsilon_{am})(\epsilon_{cd} - \epsilon_{an})}, \quad (48e)$$

$$D_6^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{wdmn}\tilde{g}_{cadb}g_{mncv}}{(\epsilon_{vc} - \epsilon_{mn})(\epsilon_{vd} - \epsilon_{mn})}, \quad (48f)$$

$$D_7^{(3)} = \sum_{m,n,c,d}' \frac{\tilde{g}_{adm n}\tilde{g}_{cwbn}g_{mncd}}{(\epsilon_{ad} - \epsilon_{mn})(\epsilon_c - \epsilon_a)} + \text{c.c.}, \quad (48g)$$

$$D_8^{(3)} = \sum_{m,n,c,d}' \frac{\tilde{g}_{cdvn}\tilde{g}_{awbn}g_{mncd}}{(\epsilon_{cd} - \epsilon_{vn})(\epsilon_v - \epsilon_m)} + \text{c.c.}, \quad (48h)$$

$$D_9^{(3)} = \sum_{m,n,c,d}' \frac{\tilde{g}_{cwmb}\tilde{g}_{danv}\tilde{g}_{mncd}}{(\epsilon_{ad} - \epsilon_{vn})(\epsilon_{vc} - \epsilon_{am})} + \text{c.c.}, \quad (48i)$$

$$D_{10}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{cdvn}\tilde{g}_{awmc}\tilde{g}_{mncd}}{(\epsilon_{ad} - \epsilon_{mn})(\epsilon_{cd} - \epsilon_{vn})} + \text{c.c.}, \quad (48j)$$

$$D_{11}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{g}_{advn}\tilde{g}_{cwdm}\tilde{g}_{mncb}}{(\epsilon_{ac} - \epsilon_{mn})(\epsilon_{ad} - \epsilon_{vn})} + \text{c.c.}, \quad (48k)$$

$$D_{12}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{damv}\tilde{G}_{cmnb}\tilde{G}_{wndc}}{(\varepsilon_{cd} - \varepsilon_{vn})(\varepsilon_{ad} - \varepsilon_{vm})} + \text{c.c.}, \quad (48l)$$

$$D_{13}^{(3)} = - \sum_{m,n,c,d} ' \frac{\tilde{G}_{wcbn}\tilde{G}_{dnmv}\tilde{G}_{madc}}{(\varepsilon_{cd} - \varepsilon_{am})(\varepsilon_{vc} - \varepsilon_{an})} + \text{c.c.}, \quad (48m)$$

$$D_{14}^{(3)} = - \sum_{m,n,c,d} ' \frac{\tilde{G}_{wdbn}\tilde{G}_{camd}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_{vd} - \varepsilon_{an})} + \text{c.c.}, \quad (48n)$$

$$D_{15}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdmn}\tilde{G}_{wnbv}\tilde{G}_{macd}}{(\varepsilon_{cd} - \varepsilon_{am})(\varepsilon_a - \varepsilon_n)} + \text{c.c.}, \quad (48o)$$

$$D_{16}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdvn}\tilde{G}_{nwm}\tilde{G}_{amcd}}{(\varepsilon_{cd} - \varepsilon_{vn})(\varepsilon_{cd} - \varepsilon_{am})} + \text{c.c.}, \quad (48p)$$

$$D_{17}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdnm}\tilde{G}_{wacd}\tilde{G}_{mnbv}}{(\varepsilon_{cd} - \varepsilon_{av})(\varepsilon_{av} - \varepsilon_{mn})} + \text{c.c.}, \quad (48q)$$

$$D_{18}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdmn}\tilde{G}_{macb}\tilde{G}_{wnvd}}{(\varepsilon_c - \varepsilon_m)(\varepsilon_d - \varepsilon_n)} + \text{c.c.}, \quad (48r)$$

$$D_{19}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{G}_{cdnv}\tilde{G}_{nwmd}\tilde{G}_{macb}}{(\varepsilon_{cd} - \varepsilon_{vn})(\varepsilon_c - \varepsilon_m)} + \text{c.c.}, \quad (48s)$$

$$D_{20}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdmn}\tilde{G}_{wabc}\tilde{G}_{mnvd}}{(\varepsilon_{vd} - \varepsilon_{mn})(\varepsilon_c - \varepsilon_v)} + \text{c.c.}, \quad (48t)$$

$$D_{21}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{adm}\tilde{G}_{cwdb}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_{ad} - \varepsilon_{mn})} + \text{c.c.}, \quad (48u)$$

$$D_{22}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{G}_{adm}\tilde{G}_{cnbd}\tilde{G}_{mwcv}}{(\varepsilon_{ad} - \varepsilon_{mn})(\varepsilon_c - \varepsilon_m)} + \text{c.c.}, \quad (48v)$$

$$D_{23}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{cdmb}\tilde{G}_{awnd}\tilde{G}_{mncv}}{(\varepsilon_{cd} - \varepsilon_{am})(\varepsilon_{vc} - \varepsilon_{mn})} + \text{c.c.}, \quad (48w)$$

$$D_{24}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{G}_{adb}\tilde{G}_{cwnd}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_d - \varepsilon_m)} + \text{c.c.}, \quad (48x)$$

$$D_{25}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{G}_{cdb}\tilde{G}_{amnd}\tilde{G}_{nwcv}}{(\varepsilon_{cd} - \varepsilon_{am})(\varepsilon_c - \varepsilon_n)} + \text{c.c.}, \quad (48y)$$

$$D_{26}^{(3)} = - \sum_{m,n,c,d} \frac{\tilde{G}_{adb}\tilde{G}_{cmnd}\tilde{G}_{nwcv}}{(\varepsilon_d - \varepsilon_m)(\varepsilon_c - \varepsilon_n)} + \text{c.c.}, \quad (48z)$$

the triple-excited states terms are

$$T_1^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{canr}\tilde{G}_{wrvm}\tilde{G}_{mncb}}{(\varepsilon_{ac} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{nr})}, \quad (49a)$$

$$T_2^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{wcmr}\tilde{G}_{arbn}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_{vc} - \varepsilon_{mr})}, \quad (49b)$$

$$T_3^{(3)} = \sum_{m,n,r,c} \frac{\tilde{G}_{canr}\tilde{G}_{rvnm}\tilde{G}_{wmbc}}{(\varepsilon_{ac} - \varepsilon_{vm})(\varepsilon_{ac} - \varepsilon_{nr})} + \text{c.c.}, \quad (49c)$$

$$T_4^{(3)} = \sum_{m,n,r,c} ' \frac{\tilde{G}_{wcrb}\tilde{G}_{arnm}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_{vc} - \varepsilon_{ar})} + \text{c.c.}, \quad (49d)$$

$$T_5^{(3)} = - \sum_{m,n,r,c} ' \frac{\tilde{G}_{warb}\tilde{G}_{crmn}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_v - \varepsilon_r)} + \text{c.c.}, \quad (49e)$$

$$T_6^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{camr}\tilde{G}_{wrnb}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{mr})} + \text{c.c.}, \quad (49f)$$

$$T_7^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{acmr}\tilde{G}_{wrnc}\tilde{G}_{mnbv}}{(\varepsilon_{av} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{mr})} + \text{c.c.}, \quad (49g)$$

$$T_8^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{carm}\tilde{G}_{mrnb}\tilde{G}_{wnvc}}{(\varepsilon_{ac} - \varepsilon_{mr})(\varepsilon_c - \varepsilon_n)} + \text{c.c.}, \quad (49h)$$

$$T_9^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{camr}\tilde{G}_{mrnc}\tilde{G}_{wnvb}}{(\varepsilon_{ac} - \varepsilon_{mr})(\varepsilon_a - \varepsilon_n)} + \text{c.c.}, \quad (49i)$$

$$T_{10}^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{carb}\tilde{G}_{wrnm}\tilde{G}_{mncv}}{(\varepsilon_{vc} - \varepsilon_{mn})(\varepsilon_c - \varepsilon_r)} + \text{c.c.}, \quad (49j)$$

$$T_{11}^{(3)} = - \sum_{m,n,r,c} \frac{\tilde{G}_{wcmr}\tilde{G}_{arnc}\tilde{G}_{mnbv}}{(\varepsilon_{av} - \varepsilon_{mn})(\varepsilon_{cv} - \varepsilon_{mr})} + \text{c.c.}, \quad (49k)$$

and the quadruple-excited state term is

$$Q^{(3)} = - \sum_{m,n,r,s} \frac{\tilde{G}_{wars}\tilde{G}_{rsmn}\tilde{G}_{mnbv}}{(\varepsilon_{av} - \varepsilon_{mn})(\varepsilon_{av} - \varepsilon_{rs})}. \quad (50)$$

In the above equations we have ordered the matrix elements for each term such that the first matrix element corresponds to the upper interaction of its Goldstone diagram, with the second and third matrix elements corresponding to the middle and lower interactions, respectively. Finally, the folded terms are

$$F_1 = -\sum'_{m,c} \frac{\tilde{g}_{wcbm}\tilde{g}_{amvc}}{(\varepsilon_{vc} - \varepsilon_{am})^2}, \quad (51a)$$

$$F_2 = -\delta_{vw} \sum_{m,c,d} \frac{g_{cdmb}\tilde{g}_{macd}}{(\varepsilon_{cd} - \varepsilon_{am})^2}, \quad (51b)$$

$$F_3 = \sum_{c,d} \frac{g_{cdvb}\tilde{g}_{awcd}}{(\varepsilon_{cd} - \varepsilon_{av})^2}, \quad (51c)$$

$$F_4 = \sum_{m,c} \frac{\tilde{g}_{camb}\tilde{g}_{wmvc}}{(\varepsilon_c - \varepsilon_m)^2} + \text{c.c.}, \quad (51d)$$

$$F_5 = -\delta_{ab} \sum_{m,n,c} \frac{g_{wcmn}\tilde{g}_{mnvc}}{(\varepsilon_{vc} - \varepsilon_{mn})^2}, \quad (51e)$$

$$F_6 = \sum_{m,n} \frac{g_{wamn}\tilde{g}_{mnvb}}{(\varepsilon_{av} - \varepsilon_{mn})^2}, \quad (51f)$$

$$F_7 = -\delta_{vw} \sum_{m,n,c} \frac{g_{acmn}\tilde{g}_{mncb}}{(\varepsilon_{ac} - \varepsilon_{mn})^2}, \quad (51g)$$

$$F_8 = -\delta_{ab} \sum_{m,c,d} \frac{g_{cdmv}\tilde{g}_{mwcd}}{(\varepsilon_{cd} - \varepsilon_{vm})^2}, \quad (51h)$$

$$F_9 = \sum_{m,c} \frac{\tilde{g}_{camv}\tilde{g}_{wmbc}}{(\varepsilon_{ac} - \varepsilon_{vm})^2}. \quad (51i)$$

Before turning to the Goldstone diagram representation of the above expressions we make the following remarks. The first is that in calculating the double-excitation terms, certain energy denominator simplifications have been made. For example, the term $D_7^{(3)}$ came from combining two terms,

$$D_{7a}^{(3)} = \sum_{m,n,c,d} \frac{\tilde{g}_{adm n}\tilde{g}_{cwbv}g_{mncd}}{(\varepsilon_{cd} - \varepsilon_{mn})(\varepsilon_{ad} - \varepsilon_{mn})} + \text{c.c.} \quad (52)$$

and

$$D_{7b}^{(3)} = \sum'_{m,n,c,d} \frac{\tilde{g}_{adm n}\tilde{g}_{cwbv}g_{mncd}}{(\varepsilon_{cd} - \varepsilon_{mn})(\varepsilon_c - \varepsilon_a)} + \text{c.c.} \quad (53)$$

which have identical numerators but denominators that can be simplified using

$$\frac{1}{A+B} \left(\frac{1}{A} + \frac{1}{B} \right) = \frac{1}{AB}. \quad (54)$$

However, care must be taken with this manipulation because it is necessary to first separate out from $D_{7a}^{(3)}$ the part of the sum where $a = c$, which leads to an ex-

tra term. The same manipulation has been used for $D_8^{(3)}$, $D_9^{(3)}$, $D_{15}^{(3)}$, $D_{17}^{(3)}$, $D_{18}^{(3)}$, and $D_{20}^{(3)}$, although when no restriction on the summation is present there is no extra term generated by the manipulation. In all, three extra terms are generated, which have been absorbed in $E_{\text{fold}}^{(3)}$ as discussed below.

Turning to the Goldstone diagrams representing these results, we note that while there are 520 diagrams associated with $E_{av}^{(3)}$ in the above expressions, we show in Figs. 2(a)–2(e) only 50 diagrams. This relatively compact form is made possible because, as discussed above, each diagram is the first of either two, four, or eight diagrams generated when one, two, or three antisymmetrized Coulomb matrix elements are present in the corresponding analytic form. Furthermore, each analytic form with a “c.c.” is associated with a diagram obtained through reflection in a horizontal plane that is not explicitly shown. Finally, the diagrams associated with the double excitations discussed above have the special feature that two orderings are possible. One could treat the orderings separately, but here we have combined them, which is indicated by a cross on the ambiguous vertex.

The terms F_1 through F_9 are obtained by the evaluation of the second term on the right-hand side of Eq. (39). In diagrammatic language, they correspond to the so-called *folded* [4] or *backwards* [6] diagrams. These diagrams exist only for open-shell systems and only for third or higher order. Brandow [4] has proposed a diagrammatic representation of these terms in which an intermediate state is replaced by an initial state, and the usual ordering of the associated interactions is reversed. These diagrams are shown in Fig. 3. Had we not combined denominators in the double-excitation terms the F_i terms could be obtained from the second-order energy expressions (excluding $E_{\text{core}}^{(2)}$) by squaring the energy denominators and changing the sign. Because we have combined denominators, the three extra terms mentioned above must be added in, and their effect is to change the signs of F_7 , F_8 , and F_9 .

V. DISCUSSION

Compared to the already somewhat complex formulas needed for one-electron outside closed-shell atoms, we see that MBPT for particle-hole states leads to very lengthy expressions. It has proved, however, relatively straightforward to create computer code to explicitly evaluate these formulas. The most important simplifying device is the treatment of terms involving \tilde{g}_{ijkl} as one object. Because up to three of these antisymmetrized Coulomb matrix elements can enter in third order, each third-order Goldstone diagram shown represents up to eight diagrams. However, all eight can be evaluated simultaneously by using the identity

$$\tilde{g}_{ijkl} = \sum_L Z_L(ijkl)J_L(ijkl), \quad (55)$$

where

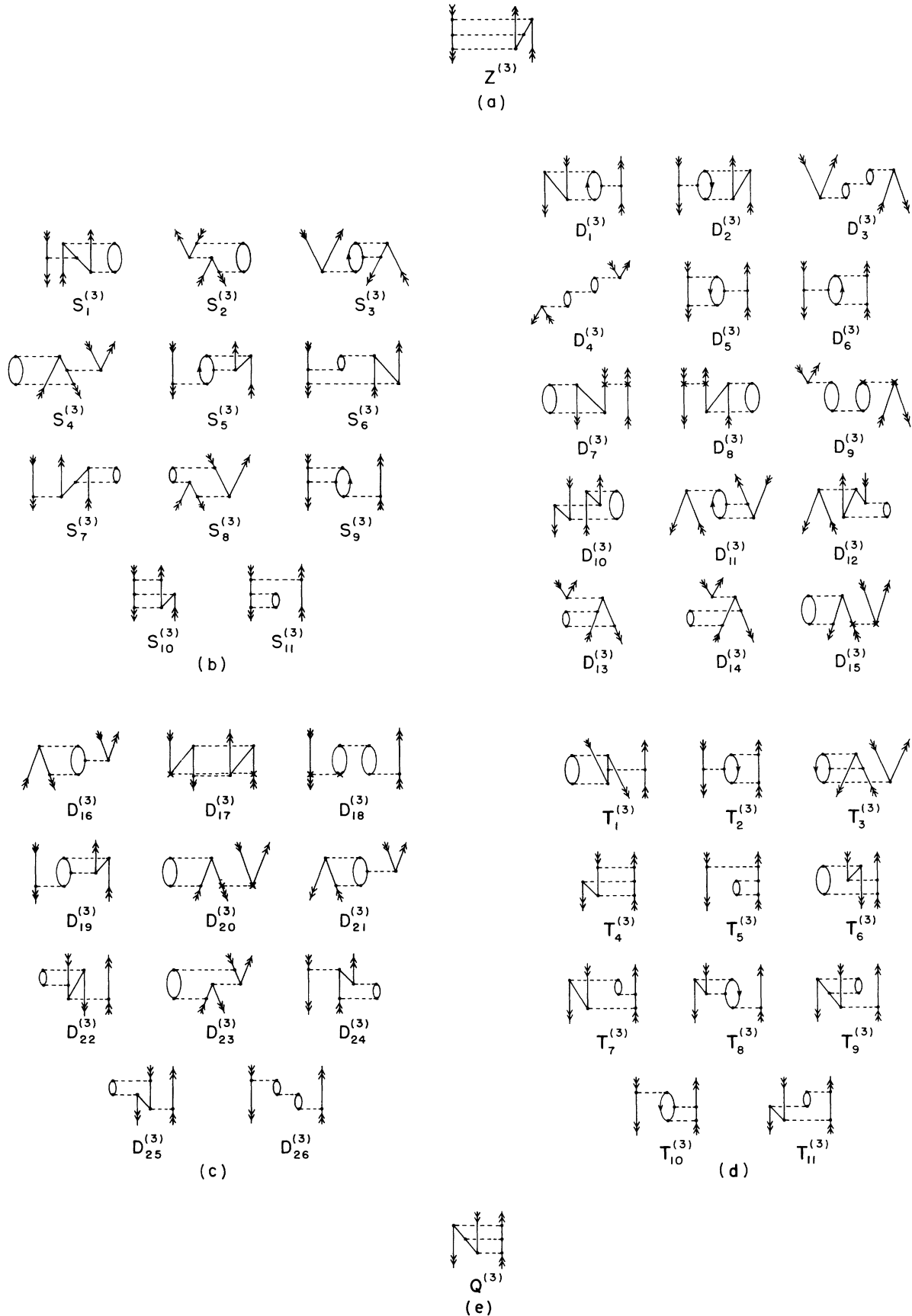


FIG. 2. Goldstone diagrams representing $E_{av}^{(3)}$ given in Eqs. (46)–(50).

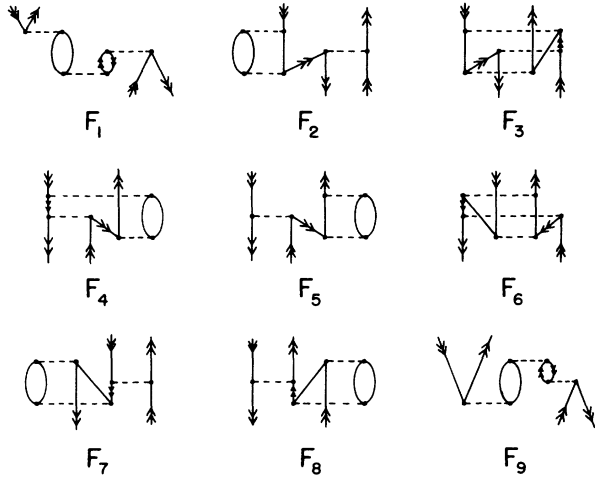


FIG. 3. Folded diagrams associated with Eq. (51).

$$Z_L(ijkl) = X_L(ijkl) + (2L+1) \sum_{L'} \begin{Bmatrix} j_j & j_i & L \\ j_i & j_k & L' \end{Bmatrix} \times X_{L'}(jikl). \quad (56)$$

$$X_L(ijkl) = (-1)^L C_L(ik) C_L(jl) \int dr \int dr' \frac{r^L}{r^{L+1}} [g_i(r)g_k(r) + f_i(r)f_k(r)][g_j(r')g_l(r') + f_j(r')f_l(r')], \quad (57)$$

where g and f are the upper and lower components of the Dirac wave functions and

$$C_J(ij) = (-1)^{j_i+1/2} \sqrt{(2j_i+1)(2j_j+1)} \begin{pmatrix} j_j & J & j_i \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}, \quad (58)$$

where the parity selection rule that $C_J(ij) = 0$ if $J+l_i+l_j$ is odd is understood.

While this reduced considerably the amount of coding, the number of terms was still so large that two completely independent angular reductions and codings were performed. In addition, in one of the codings two differ-

TABLE II. Contributions to the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy in second order for neonlike xenon: units a.u.

Term	
$E_v^{(2)}$	-0.0317
$E_a^{(2)}$	-0.0566
$Z^{(2)}$	0.0100
$S_1^{(2)}$	-0.0019
$S_2^{(2)}$	-0.0482
$S_3^{(2)}$	0.0154
$S_4^{(2)}$	0.0154
$D^{(2)}$	0.0070
Sum	-0.0906

TABLE I. MBPT contributions to the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy in neonlike xenon: units a.u.

Term	
$E^{(0)}$	159.347
$E^{(1)}$	-4.341
$E^{(2)}$	-0.091
$E^{(3)}$	0.004
$B^{(1)}$	-0.287
$B^{(2)}$	0.044
QED	0.030
Sum	154.706
Experiment ^a	154.721(5)

^aReference [9].

Here $J_L(ijkl)$ is an angular factor given in the Appendix, where we present the explicit angular reductions for the first- and second-order energies. The radial matrix element $X_L(ijkl)$ is defined as

ent angular reductions were done by reversing the orders of one or more of the \tilde{g} factors. The sums over intermediate states were carried out with standard basis-set techniques [7].

To illustrate the behavior of MBPT, we show in Table I the results of a calculation through third order of the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy in neonlike xenon, where the hole is a $2p_{3/2}$ state and the particle a $3s_{1/2}$ state. Because relativistic and QED effects are enhanced

TABLE III. Contributions to the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy of the third-order S and T terms for neonlike xenon: units a.u.

Term		Term	
$S_1^{(3)}$	-0.00030	$T_1^{(3)}$	-0.00113
$S_2^{(3)}$	-0.00585	$T_2^{(3)}$	-0.00175
$S_3^{(3)}$	0.00008	$T_3^{(3)}$	0.00007
$S_4^{(3)}$	-0.00018	$T_4^{(3)}$	0.00041
$S_5^{(3)}$	-0.00018	$T_5^{(3)}$	-0.00165
$S_6^{(3)}$	-0.00014	$T_6^{(3)}$	-0.00012
$S_7^{(3)}$	-0.00043	$T_7^{(3)}$	-0.00009
$S_8^{(3)}$	0.00094	$T_8^{(3)}$	-0.00010
$S_9^{(3)}$	-0.00014	$T_9^{(3)}$	-0.00014
$S_{10}^{(3)}$	0.00040	$T_{10}^{(3)}$	-0.00046
$S_{11}^{(3)}$	0.00000	$T_{11}^{(3)}$	0.00047
Sum	-0.00706		-0.00446

TABLE IV. Contributions to the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy of the third-order D terms for neonlike xenon: units a.u.

Term	Term	Term	Term	Term	Term
$D_1^{(3)}$	0.00058	$D_{10}^{(3)}$	-0.00002	$D_{19}^{(3)}$	0.00030
$D_2^{(3)}$	0.00015	$D_{11}^{(3)}$	-0.00002	$D_{20}^{(3)}$	0.00037
$D_3^{(3)}$	-0.00004	$D_{12}^{(3)}$	-0.00002	$D_{21}^{(3)}$	-0.00001
$D_4^{(3)}$	-0.00465	$D_{13}^{(3)}$	0.00119	$D_{22}^{(3)}$	0.00021
$D_5^{(3)}$	0.00236	$D_{14}^{(3)}$	0.00093	$D_{23}^{(3)}$	0.00099
$D_6^{(3)}$	0.00100	$D_{15}^{(3)}$	0.00021	$D_{24}^{(3)}$	0.00114
$D_7^{(3)}$	0.00000	$D_{16}^{(3)}$	-0.00004	$D_{25}^{(3)}$	0.00121
$D_8^{(3)}$	0.00049	$D_{17}^{(3)}$	-0.00007	$D_{26}^{(3)}$	-0.00005
$D_9^{(3)}$	-0.00013	$D_{18}^{(3)}$	-0.00109		
Sum					0.00499

in highly charged ions we have included the lowest-order Breit interaction $B^{(1)}$ (including frequency dependence) and the first-order Coulomb correction to it, $B^{(2)}$, along with an estimate of QED effects from Grant's multiconfiguration Dirac-Fock (MCDF) program [8] and a comparison with experiment [9]. For highly charged ions the n th level of perturbation theory is accompanied by a factor Z^{2-n} . As can be seen from Table I, this leads to a relatively small value for $E^{(3)}$, while $E^{(2)}$ is large enough so that it must be quite accurately calculated in order to compare with experiment. Its detailed breakdown is given in Table II. The largest contributions to $E^{(2)}$ are seen to come from $E_a^{(2)}$ and $S_2^{(2)}$, although the only very small contribution is $S_1^{(2)}$. A high-accuracy evaluation of $E^{(2)}$, with large basis sets and an accurate treatment of the partial-wave summations, can be carried out in a matter of minutes on an IBM RISC/6000 workstation.

Turning to the third-order calculation, we present the breakdown of the S and T terms in Table III, the D terms in Table IV, and the complete set of contributions to $E^{(3)}$ in Table V. As can be seen from Table V, $E_a^{(3)}$ continues to dominate $E_v^{(3)}$. However, significant contributions also come from a large number of $E_{av}^{(3)}$ terms as well as $E_{\text{fold}}^{(3)}$, and we have not been able to identify any one class of diagrams that dominate the result. However, the complete third-order calculation can be carried out in a few hours, with the bulk of the computation involving the quadruple excitation terms.

The comparison with experiment in Table I shows a 0.015-a.u. discrepancy, which is three times the exper-

TABLE V. Summary of $E^{(3)}$ calculation of the $(2p^5 3s_{1/2})_{J=2} \rightarrow 2p^6$ transition energy in neonlike xenon: units a.u.

Term	Term
$E_v^{(3)}$	0.00025
$E_a^{(3)}$	0.00340
$Z^{(3)}$	-0.00050
$S^{(3)}$	-0.00706
$D^{(3)}$	0.00499
$T^{(3)}$	-0.00446
$Q^{(3)}$	-0.00017
$E_{\text{fold}}^{(3)}$	0.00708
Sum	0.00353

imental error bar. Given the rapid pattern of convergence of the $E^{(i)}$ terms, it is unlikely that $E^{(4)}$ could account for this. More likely is some combination of the neglect of $B^{(3)}$ or the fact that the QED term was obtained phenomenologically. We are at present examining with the formulas derived in this paper the helium, beryllium, neon, and magnesium isoelectronic sequences and working on identifying a dominant part of $B^{(3)}$ and calculating QED effects from first principles. When this has been done it should be possible to extend the understanding of the physics of one-valence electron ions studied in Ref. [2] to the richer spectrum of particle-hole excitations of closed-shell systems.

ACKNOWLEDGMENTS

We would like to thank J.E. Hansen, A.E. Livingston, and G. Serpa for useful conversations. This research was supported in part by NSF Grant No. PHY-90-12408. W.R.J. and J.S. would like to acknowledge the hospitality of Lawrence Livermore National Laboratory, where some of their work was carried out.

APPENDIX

Before any of the formulas presented in this paper can be evaluated, it is necessary to first perform an angular reduction. This involves summing products of the angular factors $J_L(ijkl)$ over all magnetic quantum numbers, where

$$J_L(ijkl) = \sum_M (-1)^{j_i+j_j+L-m_i-m_j-M} \begin{pmatrix} j_i & L & j_k \\ -m_i & M & m_k \end{pmatrix} \begin{pmatrix} j_j & L & j_l \\ -m_j & -M & m_l \end{pmatrix}. \quad (\text{A1})$$

That summation can be carried out with the graphical techniques described in Ref. [1]. The results for the first- and second-order energies are

$$E^{(1)} = - \sum_L (-1)^{J+j_a+j_v} \begin{Bmatrix} j_v & j_a & J \\ j_a & j_v & L \end{Bmatrix} Z_L(vava) \quad (\text{A2})$$

and

$$E_v^{(2)} = \sum_{[m,n,c],L} (-1)^{j_v+j_c+j_m+j_n} \frac{1}{2L+1} \frac{1}{2j_v+1} \frac{X_L(vcmn)Z_L(mnvc)}{\epsilon_{cv} - \epsilon_{mn}} \quad (\text{A3})$$

$$- \sum_{[m,c,d],L} (-1)^{j_c+j_d+j_v+j_m} \frac{1}{2L+1} \frac{1}{2j_v+1} \frac{X_L(cdvm)Z_L(vmcd)}{\epsilon_{cd} - \epsilon_{mv}}, \quad (\text{A4})$$

$$E_a^{(2)} = - \sum_{[m,n,c],L} (-1)^{j_a+j_c+j_m+j_n} \frac{1}{2L+1} \frac{1}{2j_a+1} \frac{X_L(camn)Z_L(mnca)}{\epsilon_{ac} - \epsilon_{mn}} \quad (\text{A5})$$

$$+ \sum_{[m,c,d],L} (-1)^{j_a+j_c+j_d+j_m} \frac{1}{2L+1} \frac{1}{2j_a+1} \frac{X_L(cdvm)Z_L(madc)}{\epsilon_{cd} - \epsilon_{ma}}, \quad (\text{A6})$$

$$Z^{(2)} = - \sum_{[c,d],L_1,L_2} (-1)^{J+j_a+j_v} \left\{ \begin{matrix} j_a & J & j_v \\ L_1 & j_c & L_2 \end{matrix} \right\} \left\{ \begin{matrix} L_2 & L_1 & J \\ j_a & j_v & j_d \end{matrix} \right\} \frac{X_{L_1}(cdva)Z_{L_2}(vadc)}{\epsilon_{cd} - \epsilon_{av}}, \quad (\text{A7})$$

$$S_1^{(2)} = \sum_{[m,c]} (-1)^{j_a+j_v+j_c+j_m} \frac{1}{(2J+1)^2} \frac{Z_J(camv)Z_J(vmac)}{\epsilon_{ac} - \epsilon_{mv}}, \quad (\text{A8})$$

$$S_2^{(2)} = \sum'_{[m,c]} (-1)^{j_a+j_v+j_c+j_m} \frac{1}{(2J+1)^2} \frac{Z_J(macv)Z_J(vcam)}{\epsilon_{vc} - \epsilon_{ma}}, \quad (\text{A9})$$

$$S_3^{(2)} + S_4^{(2)} = 2 \sum_{[m,c],L} (-1)^{J+L+j_a+j_v+j_c+j_m} \frac{1}{2L+1} \left\{ \begin{matrix} j_v & j_a & J \\ j_a & j_v & L \end{matrix} \right\} \frac{Z_L(cvmv)Z_L(maca)}{\epsilon_c - \epsilon_m}, \quad (\text{A10})$$

$$D^{(2)} = - \sum_{[m,n],L_1,L_2} (-1)^{J+j_a+j_v} \left\{ \begin{matrix} j_a & J & j_v \\ L_1 & j_n & L_2 \end{matrix} \right\} \left\{ \begin{matrix} L_2 & L_1 & J \\ j_a & j_v & j_m \end{matrix} \right\} \frac{X_{L_1}(nmva)Z_{L_2}(vamn)}{\epsilon_{mn} - \epsilon_{av}}. \quad (\text{A11})$$

A square bracket in the above equations indicates that the magnetic quantum number has already been summed over. It is a straightforward, though lengthy exercise to do the angular reductions of the third-order energy.

-
- * Present address: DRF/Service de Physique Atomique, CENG, Boîte Postale 85X, F-38041 Grenoble CEDEX, France.
- [1] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).
- [2] W.R. Johnson, S.A. Blundell, and J. Sapirstein, *Phys. Rev. A* **37**, 2764 (1988); **38**, 2699 (1988); **42**, 1087 (1990).
- [3] S.A. Blundell, D.S. Guo, W.R. Johnson, and J. Sapirstein, *At. Data Nucl. Data Tables* **37**, 103 (1987).
- [4] B.H. Brandow, *Rev. Mod. Phys.* **39**, 771 (1967).
- [5] S.A. Blundell, W.R. Johnson, and J. Sapirstein, *Phys. Rev. A* **42**, 3751 (1990).
- [6] P.G.H. Sandars, *J. Phys. B* **10**, 2983 (1977).
- [7] W.R. Johnson, S.A. Blundell, and J. Sapirstein, *Phys. Rev. A* **37**, 307 (1988).
- [8] I.P. Grant, B.J. McKenzie, P.H. Norrington, D.F. Mayers, and N.C. Pyper, *Comput. Phys. Commun.* **21**, 207 (1980).
- [9] P. Beiersdorfer, S. von Goeler, M. Bitter, E. Hinnov, R. Bell, S. Bernabei, J. Felt, K.W. Hill, R. Hulse, J. Stevens, S. Suckewer, J. Timberlake, A. Wouters, M.H. Chen, J.H. Scofield, D.D. Dietrich, M. Gerassimenko, E. Silver, R.S. Walling, and P.L. Hagelstein, *Phys. Rev. A* **37**, 4153 (1988).