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Correlation Energy of Atomic Nitrogen[†]

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The Brueckner-Goldstone many-body perturbation theory is applied to study the electronic structure of the atomic nitrogen in its ground ^4S state. A complete orthonormal set of the V^{N-1} single-particle states with angular symmetry up to $l = 5$ is explicitly used to calculate the correlation-energy diagrams. The contribution from higher l (> 5) is estimated by a hydrogenic approximation of the continuum wave functions. Our final correlation energy is -0.1895 ± 0.003 a.u., as compared with -0.1886 ± 0.0094 a.u. from the semiempirical estimate made by Veillard and Clementi. The sum of the exchange-core-polarization and pair-correlation-energy diagrams give a total of -0.20728 a.u., which is 110% of the semiempirical estimate. This contains a contribution of -0.00610 a.u. (3.2 %) from $l > 3$ states and -0.05825 a.u. (31 %) from the excitations into the valence $2p$ orbitals, the latter arising from the open-shell nature of the nitrogen atom. The overestimate (10 %) of the correlation energy is remedied by the pair-pair correlation of 0.01137 a.u. (6%) and the many-electron (three and four) effect of 0.00642 a.u. (3.4 %). A comparison with earlier configuration-interaction results is also made.

I. INTRODUCTION

The Hartree-Fock (HF) theories are known to yield accurate total energies of the neutral species of light atoms and molecules in the one-electron approximation. However, the total energies are usually of little physical or chemical interest. For example, the chemical dissociation energies of molecules or spectroscopic excitation energies of atoms are usually small numbers arising out of differences between the large total energies in which the role of correlation energy is vital. The correlation energy is customarily defined as the difference between the exact nonrelativistic energy and the restricted Hartree-Fock (RHF) energy. Recently, considerable efforts have been made in calculation of the correlation energies of many atoms.[1] Basically, these could be classified into two broad categories. First is the variational approach in which the many-electron Schrödinger equation is solved by configuration-interaction (CI) method using a finite and discrete basis set. This is usually carried out in the framework of single and double excitations of electrons starting from the RHF wave function. However, in order to obtain quantitatively accurate results, such approaches usually need to employ a very large and sufficiently flexible basis set, which is often computationally difficult and expensive. Also, the criterion for choosing a proper basis set is not always clear cut as one can not always meet fully the demand for the completeness of a basis set.

An alternate approach which circumvents these difficulties is the many-body perturbation theory (MBPT).[2] This has been successfully applied to compute the correlation energies[3,4] as well as other properties of atoms.[5] An attempt was recently made to establish a direct contact between these two approaches for the case of correlation energy in the atomic neon.[4] In the present work, we analyze the correlation energy of the atomic nitrogen in its ground ^4S state by MBPT. There are several reasons for undertaking this calculation. First, it has been demonstrated that the sum of independently calculated pair-correlation energy $e(p, q)$ by either variation or perturbation approach usually yields an overestimate of the correlation energy, the main reason for this being the neglect of the pair-pair interaction.[4,6-10] A full CI calculation will of course include the pair-pair interaction automatically. This is, however, very seldom performed even for light atoms, because of obvious computational limitations.

Secondly, inclusion of orbitals of higher angular symmetry ($l > 3$) is found by no means negligible.[6,7] However, a considerable amount of cancellation is observed between these two contributions in the case of the atomic neon. It is interesting to investigate whether this kind of cancellation occurs in general. A study of the electron correlation in the atomic nitrogen can provide a clue to these questions and help to understand the electronic structure of neutral atoms in general. In addition, nitrogen being an open-shell atom provides other interesting features occurring due to mixing of the single- and double-excitation configurations. Also, the earlier calculation of Nesbet by the Bethe-Goldstone method[11] and the recent result of Platas and Schaefer[12] by a symmetry-adapted pair-correlation calculation (SAPCI) will enable us to carry out comparisons of the results obtained by different methods. Finally, we can make use of the same basis set and matrix elements which were utilized in our earlier work on the hyperfine interaction of this atom.[5]

In Sec. II, a brief review of MBPT and analysis of diagrams are presented. The computational aspect of the problem together with the results is given in Sec. III. Comparison of the present work with earlier CI calculations is carried out in Sec. IV. Section V contains the summary and conclusions obtained from the present work.

II. METHOD

Since the details of MBPT have been given at length elsewhere,[2,5] we will present here only the barest essentials necessary for the subsequent discussion. The total nonrelativistic Hamiltonian $\mathcal{H}$ for an N electron atom is given by the sum of the unperturbed Hamiltonian $\mathcal{H}_0$ and the perturbation $\mathcal{H}'$ defined by

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}' , \tag{1}$$

where

$$\mathcal{H}_0=\sum_{i=1}^{N}(T_i+V_i) , \tag{2}$$

$$\mathcal{H}'=\sum_{i>j}^{N}v_{ij}-\sum_{i=1}^{N}V_i . \tag{3}$$

T_i is the sum of the kinetic energy and nuclear attraction terms, and v_{ij} is the Coulomb repulsion between ith and jth electrons. V_i is an appropriately chosen single-particle potential. Hartree units are used everywhere.[13] In this work the V^{N-1} potential is employed.[5] A complete orthonormal set of single-particle states $\{\varphi_n\}$ is generated by solving

$$(T+V)\varphi_n=\epsilon_n\varphi_n . \tag{4}$$

Both bound and continuum states are included. Explicit equations for the reduced radial wave functions for the s, p, and d states are given in our earlier work.[5] The f, g, and h states are obtained by solving the following equation:

$$\begin{aligned}\epsilon_{nl}P(nl;r)=&\left(\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}-4\,\frac{Y_0(1s^0,1s^0;r)}{r}-4\,\frac{Y_0(2s^0,2s^0;r)}{r}-4\,\frac{Y_0(2p^0,2p^0;r)}{r}\right.\\&\left.+a_l\,\frac{Y_2(2p^0,2p^0;r)}{r}\right)P(nl;r)+\frac{2}{2l+1}\left(\frac{Y_l(1s^0,nl;r)}{r}\,P(1s^0;r)+\frac{Y_l(2s^0,nl;r)}{r}\,P(2s^0;r)\right)\\&+b_{l-1}\,\frac{Y_{l-1}(2p^0,nl;r)}{r}\,P(2p^0;r)+b_{l+1}\,\frac{Y_{l+1}(2p^0,nl;r)}{r}\,P(2p^0;r) .\end{aligned} \tag{5}$$

The notations are consistent with those used in our earlier work. The coefficients in front of the direct and exchange terms in Eq. (5) arise out of the appropriate spherical averaging of the V^{N-1} potential. They are given in Table I. Thus, all s states are computed in the field of the nucleus, two 1s electrons, one 2s electron, and three 2p electrons, whereas non-s states ($l\neq0$) are generated in the field which includes interaction with the nucleus, two 1s electrons, two 2s electrons, and two 2p electrons. Therefore, the 2s and 2p states are the HF states, whereas 1s does not correspond to the HF 1s state, denoted by $1s^0$. Consequently, the single-particle energy ϵ_{1s} is different from the HF 1s energy, although the wave functions do not differ significantly. The unperturbed ground state Φ_0 is taken to be a single Slater determinant composed of the 1s, 2s, and 2p orbitals obtained from Eqs. (12) and (14) in Ref. 5. The states included in Φ_0 are called unexcited states and the rest are called excited states. It is reminded that these excited states do not imply the physical excited states of the system. Following the usual convention, the unoccupied unexcited states are called holes, whereas the occupied excited states are called particles.[2] The exact nonrelativistic total energy E is given by the following perturbation series:

$$E=E_0+\sum_{n=0}^{\infty}\langle\Phi_0|\mathcal{H}'\left(\frac{Q}{E_0-\mathcal{H}_0}\,\mathcal{H}'\right)^n|\Phi_0\rangle_L , \tag{6}$$

with

$$E_0=\sum_{i=1}^{N}\epsilon_i . \tag{7}$$

TABLE I. Coefficients a_l and b_l in Eq. (5).

l	a_l	b_{l-1}	b_{l+1}
3	1.7778×10^{-2}	0.274 28	0.282 18
4	1.0390×10^{-2}	0.217 69	0.220 39
5	6.8376×10^{-4}	0.179 57	0.180 74

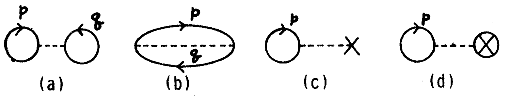

FIG. 1. First-order corrections to the uperturbed energy. The dotted line represents v_{ij} interaction, whereas the dotted line terminating with a cross denotes the interaction with the single-particle potential V. Figure (d) represents the net sum of interactions in (a), (b), and (c), viz., (a) + (b) + (c) = (d).

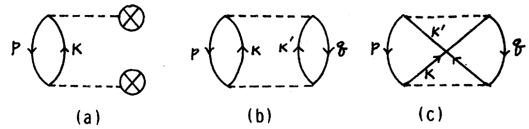

FIG. 2. Second-order correlation-energy diagrams.

The operator Q removes the Φ_0 component and ensures no Φ_0 contribution to the intermediate states. The subscript L indicates that only "linked" terms should be included in the sum.[2] If the RHF basis set is used, the sum of E_0 and the $n=0$ term in Eq. (6) will give the RHF energy.

We follow the usual diagrammatic procedure to evaluate the various terms in Eq. (6). Figures 1(a)-1(c) describe the first-order diagrams which represent corrections to E_0 due to interaction between electrons in the passive unexcited states and also with the single-particle potential V. Since these three types of interactions appear repeatedly in the subsequent diagrams, we use the compact symbol given in Fig. 1(d) to denote the net effect V_{eff} due to Figs. 1(a)–1(c). The mathematical expression for the interaction in Fig. 1(d) is then given by

$$\langle p \,|\, V_{\text{eff}} \,|\, p\rangle = \sum_{q=1}^{N} [pq\,|v_{ij}|\,pq] - \langle p \,|\, V \,|\, p\rangle \,, \tag{8}$$

where

$$[pq\,|v_{ij}|\,pq] = \langle pq\,|v_{ij}|\,pq\rangle - \langle pq\,|v_{ij}|\,qp\rangle\, \delta_{m_{si}\, m_{sj}}$$

It is observed that whenever $p=1s$, we obtain an additional correction term resulting from Fig. 1(d):

$$\Delta\epsilon_{1s} = [1s\; 2s\,|v_{ij}|\,1s\; 2s] + \langle 1s\; 1s\,|v_{ij}|\,1s\;\; 1s\rangle - 2\langle 1s\; 1s^0\,|v_{ij}|\,1s\; 1s^0\rangle + \langle 1s\; 1s^0\,|v_{ij}|\,1s^0 1s\rangle \,. \tag{9}$$

The last three terms in Eq. (9) result from the difference between the $1s$ and $1s^0$ wave functions. The sum of E_0 and contributions from the first-order diagrams gives the RHF energy.

In Fig. 2, all second-order diagrams are presented. Figure 2(a) represents the effect of the single-excitation contribution to the energy. If the unrestricted Hartree-Fock (UHF) basis set is used, the net contribution from this diagram is zero. However, since we have used the RHF basis set and because the nitrogen atom is an open-shell system, this diagram survives whenever the hole state p is either the $1s$ or $2s$ state. The physical effect represented by this diagram is the unsymmetrical exchange interaction between spin-up and spin-down core s electrons and the spin-up $2p$ electrons. This corresponds to the exchange-core-polarization (ECP) effects.[14] The expression for this diagram is given by

$$e^0(p) = {\sum_k}' \frac{|\langle p \,|\, V_{\text{eff}} \,|k\rangle|^2}{\epsilon_p - \epsilon_k} \,. \tag{10}$$

The summation is understood to include a discrete sum over the bound excited states and integration over the continuum states with an appropriate density-of-state factor in the latter case. The prime in the sum implies that k excludes the unexcited states. There is a further modification to this diagram owing to the correlation shown in Fig. 3(h) and its three other time-ordered versions. This will be discussed shortly. Figure 2(b) and its exchange counterpart Fig. 2(c) represent the second-order pair correlation between p and q electrons. The expression for Fig. 2(b) is

$$e^0(p,\, q) = \sum_{k,k'}{}' \frac{|\langle pq\,|v_{ij}|\,kk'\rangle|^2}{D_{pq;\,kk'}} \,, \tag{11}$$

where

$$D_{pq;\,kk'} = \epsilon_p + \epsilon_q - \epsilon_k - \epsilon_{k'} \,. \tag{12}$$

A similar expression for the exchange diagram [Fig. 2(c)] can also be written down.

In Fig. 3, the diagrams representing the modifications to the parent diagrams 2(a)–2(c) are presented. Figure 3(a) with $p = 1s$ and $2s$ represents the effect of the splitting of the energy levels of ϵ_{1s^+} and ϵ_{1s^-} and similarly ϵ_{2s^+} and ϵ_{2s^-} on the pair-correlation energy $e(p,\, q)$. This is again due to the open-shell nature of the nitrogen atom. Interactions of the type in Fig. 3(a) are summed to all orders ex-

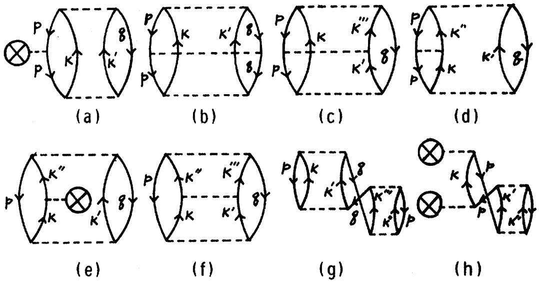

FIG. 3. Modifications to the second-order pair correlation energy of electron pair p, q and ECP diagrams.

actly by a geometric series sum, which in the present case leads to the shift in the single-particle energies ϵ_{1s} and ϵ_{2s} to

$$\epsilon^{\pm}_{ns} = \epsilon_{ns} \pm \tfrac{3}{2} \langle ns\, 2p \,|v_{ij}|\, 2p\, ns\rangle, \quad n = 1 \text{ or } 2 \tag{13}$$

where ϵ_{1s} already includes the correction $\Delta\epsilon_{1s}$ given by Eq. (9).

Figure 3(b) is the familiar hole-hole (hh) interaction. Hole-particle (hp) interactions are shown in Figs. 3(c)–3(e). There are also similar hp diagrams in which the middle interaction is attached to the q-hole side. Considerable cancellation occurs among these diagrams. For example, if the excited state k is generated in a potential in which an interaction with the hole state p is missing, then Figs. 3(d) and 3(e) cancel. Particle-particle (pp) interactions are shown in Fig. 3(f). All possible exchange counterparts of Figs. 3(a)–3(f) are also included.

The correlation-energy calculation is significantly improved if a Brillouin-Wigner-type denominator, namely, the exact energy difference of the ground and excited states of the system, is used in Eq. (11), rather than the bare single-particle energies.[15] This is partly accomplished by the inclusion of Figs. 3(b)–3(f) and their respective higher-order counterparts. They modify the second-order pair-correlation energy $e^0(p, q)$. Figures 3(b)–3(f) include the diagonal terms, namely, $k = k''$ and $k' = k'''$, as well as the nondiagonal terms. The diagonal terms are summed to infinite orders by the shifted energy denominator[15] given by

$$\begin{aligned} D'_{pq;kk'} = D_{pq;kk'} &- [pq\,|v_{ij}|\,pq] + [pk'\,|v_{ij}|\,pk'] \\ &+ [qk\,|v_{ij}|\,qk] + [pk\,|v_{ij}|\,pk] + [qk'\,|v_{ij}|\,qk'] \\ &- \langle k\,|V_{\text{eff}}|\,k\rangle - \langle k'\,|V_{\text{eff}}|\,k'\rangle - [kk'\,|v_{ij}|\,kk']. \end{aligned} \tag{14}$$

Thus, the second-order pair-correlation energy $e^0(p, q)$ corresponding to Fig. 2(b) is modified to

$$e'(p, q) = {\sum}'_{kk'} \frac{|\langle pq\,|v_{ij}|\,kk'\rangle|^2}{D'_{pq;kk'}} . \tag{15}$$

Figure 3(g) and its three other time-ordered versions violate the exclusion principle and are called "rearrangement" diagrams.[2] They represent the self-coupling of the pair (p, q). This effect is included to all orders by further shifting the energy denominator $D'_{pq;kk'}$ given by Eq. (14) to

$$D''_{pq;kk'} = D'_{pq;kk'} + e'(p, q) . \tag{16}$$

Figure 3(h) and its various time-ordered versions represent modification to the basic UHF diagram [Fig. 2(a)], because of the coupling between one- and two-electron effects. It was pointed out by Heine[16] that in variational UHF calculations, while trying to make the spin orbitals different from one another because of the unsymmetrical exchange interaction between the core and valence electrons, one introduces an inadvertent amount of correlation. This effect is demonstrated in diagrams of the type 3(h). In perturbation theory, it is possible to sum these diagrams exactly to all orders. When these diagrams are combined with Fig. 2(a), we obtain the modified ECP contribution given by

$$e'(p) = \sum_k{}' \frac{|\langle p\,|V_{\text{eff}}|\,k\rangle|^2}{\epsilon_p - \epsilon_k + \sum_{q\neq p} e(p, q) + \sum_{q\neq p} \delta^k_{p,q}} , \tag{17}$$

where

$$\delta^k_{p,q} = \sum_{k'k''}{}' \frac{|\langle pq\,|v_{ij}|\,k'k''\rangle|^2 (\epsilon_p - \epsilon_k)}{(D'_{pq;k'k''})^2} , \tag{18}$$

and $e(p, q)$ is the final pair-correlation energy obtained in the present calculation.

In Figs. 4(a)–4(g), we present the diagrams which contribute to the "pair-pair" interactions because they describe interactions between the initial and final states involving different pairs. The importance of these interactions was discussed in earlier work on atomic neon.[4] We can only evaluate the contribution from these diagrams order by order, and in the present case, they are calculated exactly until the third order. However, since the "ring" diagrams shown in Figs. 4(d) and 4(e) are found to be more important than the remaining diagrams, especially for electrons in the L shell, we have incorporated their higher-order effects such as Figs. 4(h) and 4(i) to all orders, assuming that the geometric series behavior between the contributions from subsequent orders holds approximately.

In Fig. 5, diagrams which represent many-electron (more than two) effects are presented. In this

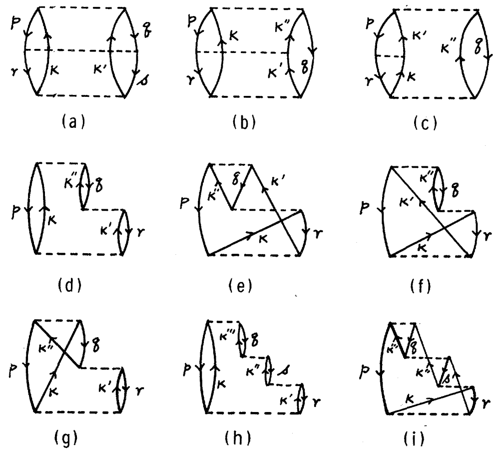

FIG. 4. Pair-pair interaction diagrams. In these figures p, q, r, and s refer to distinctly different hole states. Figure (a) describes the "nondiagonal" hole-hole interaction, whereas (b) and (c) are the "nondiagonal" hole-particle diagrams. Remaining diagrams are termed as "ring" diagrams.

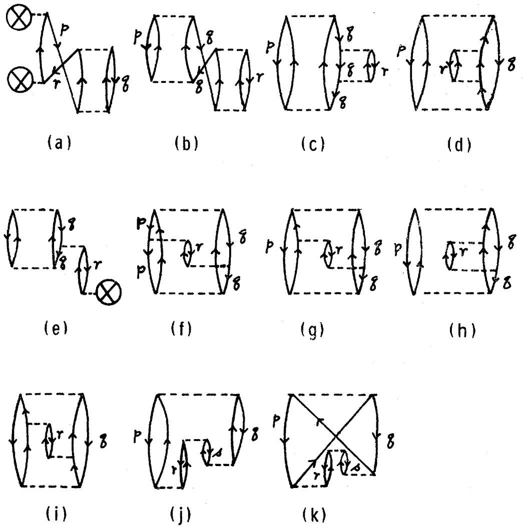

FIG. 5. Diagrams representing three- and four-electron effects.

context, we have followed the convention that an n-electron diagram will be one in which there are n distinct hole lines simultaneously present at one instant. Thus, Figs. 5(a)–5(i) represent the three-electron contribution to the correlation energy, while those of the type 5(j)–5(k) represent the four-electron contribution. Figures 5(a), 5(b), and their various time-ordered versions are rearrangement diagrams. Figure 5(a) is the many-body correction to ECP, while Fig. 5(b) represents a correction to the correlation energy $e(p, q)$ owing to three-or-more-particle effects. The latter many-electron correction is included by further shifting the energy denominator of Eq. (11) to

$$D'''_{pq;kk'} = D''_{pq;kk'} + \sum_{r\neq p} e'(q, r) + \sum_{r\neq q} e'(p, r) \; . \qquad (19)$$

Figures 5(c) and 5(d) are also rearrangement diagrams and were first considered by Bethe in nuclear matter.[17] They contribute to the self-energies of electrons in the hole and particle states. Figures 5(e)–5(i) and variations describe the screening of the interactions between electrons in the hole and particle states. For example, Fig. 5(e) shows that the single-particle potential $V_{\rm eff}$ excites a hole-particle pair, which is then annihilated by scattering a hole. This contributes to the screening of $V_{\rm eff}$ to the hole state q. This diagram exists only for $r = 1s$ or $2s$. Similarly, Figs. 5(f), 5(g) and 5(h), and 5(i) represent the effect of screening the interaction between hh, hp, and pp states, respectively. All these diagrams were neglected in earlier calculations on atomic correlation energies. They are explicitly computed and included in the present work up to fourth order. Figures 5(j) and 5(k) have also been calculated up to fourth order, for the purpose of estimating the four-electron contribution.

III. RESULTS

A. Exchange-Core Polarization

The second-order contribution owing to the ECP effect as described in Fig. 2(a) and Eq. (10) is found to be -0.00319 a.u. This is composed of -0.00080 a.u. from $1s-ks$ and -0.00239 a.u. from $2s-ks$ excitations. The modification by the rearrangement diagram 3(h) and its time-ordered variations leads the ECP value to -0.00302 a.u. This is obtained by using Eq. (17).

B. Pair-Correlation Energy

Figures 2(b) and 2(c) represent the second-order pair-correlation contributions to the energy. Their contributions are listed in the second and the third columns of Table II. These values are obtained from Eq. (11), including the modification given by Eqs. (9) and (13). In the present work, contributions from all the excited states until angular momentum $l = 5$ are explicitly evaluated. For each l value, bound excited states until $n = 10$ are explicitly calculated and contribution from states with $n > 10$ are approximated by the $n^{-3/2}$ rule.[2] For integration over the continuum states, the 12-point Gauss-Laguerre quadrature, scaled to the maximum linear momentum $k_{\rm max} = 20$ a.u., is used. The values given in the second column include l up to 3, while the values in the third column include higher l contributions. The contributions from $l > 5$ are included in an approximate manner using hydrogenic continuum states as discussed below. We notice that among all pairs of electrons, those belonging to the same shell (intrashell) correlate stronger than those in the different shell (intershell). Thus, the intrashell correlation for $1s$ (or $2s$) is much larger than the $1s$-$2s$ intershell correlation. This is understood from the fact that a $2s$ electron has a maximum radial density far from that of a $1s$ electron, and consequently its correlation with a $1s$ electron is small. Among the intershell correlations of $1s$-$2p$ and $2s$-$2p$ types, the $2s$-$2p$ correlation is larger

TABLE II. Second-order pair-correlation energy $e^0(p, q)$ for various pairs. Table is based on contributions from Figs. 2(b) and 2(c).

	$e^0(p,q)$ (a.u.)	
Pairs (p, q)	$l \leq 3$	All l
$1s$, $1s$	-0.04671	-0.04671
$1s$, $2s$	-0.00588	-0.00588
$2s$, $2s$	-0.01584	-0.01677
$1s$, $2p$	-0.01171	-0.01171
$2s$, $2p$	-0.10864	-0.11266
$2p$, $2p$	-0.04934	-0.05049
Total	-0.23812	-0.24422

TABLE III. Contribution to second-order L-shell pair-correlation energy from various excited states.

Interacting pairs	l, l of excited states	Contributions (a.u.)
$(2s,\ 2s)$	s, s	-0.00373
	p, p	-0.00471
	d, d	-0.00593
	f, f	-0.00147
	g, g	-0.00032
	h, h	-0.00019
	Higher l l'	-0.00042[a]
Subtotal		-0.01677
$(2s,\ 2p)$	$(s,p)+(p,s)$	-0.03022
	$(p,d)+(d,p)$	-0.06437
	$(d,f)+(f,d)$	-0.01405
	$(f,g)+(g,f)$	-0.00242
	$(g,h)+(h,g)$	-0.00090
	Higher l, l'	-0.00070[a]
Subtotal		-0.11266
$(2p,\ 2p)$	s, s	0
	p, p	-0.01916
	d, d	-0.02364
	f, f	-0.00654
	g, g	-0.00071
	h, h	-0.00034
	Higher l, l'	-0.00010[a]
Subtotal		-0.05049
Total L-shell correlation		-0.17992

[a] Estimated by using a hydrogenic approximation of the continuum states.

than the $1s$-$2p$ correlation, since the overlap between the $2s$ and $2p$ radial functions is larger than that between the $1s$ and $2p$. Further, the $2s$-$2p$ correlation is larger than the $2p$-$2p$ correlation by almost a factor of 2. In order to understand this qualitatively, it is recalled that the HF method partially correlates electrons with the same spins (precorrelation).[18] Since all $2p$ electrons have parallel spins, the precorrelation in the HF calculation takes care of most of the correlation between $2p$ electrons. Thus, a larger correlation between the $2s$ and $2p$ electrons than the $2p$-$2p$ electrons is expected, since no account of precorrelation between the $2s$-$2p$ pair has been taken.

In Table III, the second-order pair-correlation energy for the L-shell electrons are decomposed according to the orbital angular momenta l and l' of the excited states. The most slowly convergent pair is the $2s$-$2p$ pair, which is also found to give the dominant contribution. The major contribution in this case arises from $(2s,\ 2p)\rightarrow(kp,\ k'd)$ and $(2s,\ 2p)\rightarrow(kd,\ k'p)$ excitations. Also, the main contribution (more than 90%) to these and as well as other pairs in each excitation comes from the continuum wave functions. In view of these, we tried to estimate the contributions from continuum states with $l>5$. This is done in the following manner. The approximate form of the continuum wave functions can be written as[19]

$$P(kl\,;r)\rightarrow\frac{(2k)^l}{(2l+1)!}\,r^{l+1}e^{-ikr}F(i/k+l+1,\ 2l+2,\ 2ikr)\,,$$

where $F(i/k+l+1,\ 2l+2,\ 2ikr)$ is the confluent hypergeometric series. Since the major contribution from continuum states comes from small k values (0–1 a.u.), we further approximate $P(kl\,;r)$ by

$$P(kl\,;r)\underset{k\rightarrow 0}{\rightarrow}(2r)^{1/2}J_{2l+1}(8r)^{1/2}\,.$$

This is normalized by noticing

$$P(kl\,;r)\underset{\substack{k\rightarrow 0\\ r\rightarrow\infty}}{\rightarrow}(2r/\pi^2)^{1/4}\sin[(8r)^{1/2}-l\pi-\tfrac{1}{4}\pi]\,.$$

Therefore, the radial double-excitation matrix elements reduce to familiar integrals involving Bessel functions and hole states for which, in this case, Clementi's analytic forms[20] are used. The estimated contribution from $l>5$ states for the L-shell electrons is found to be -0.00122 a.u., which is about 0.7% of the total L-shell correlation energy.

Next we turn to the discussion of the modification to the pair-correlation energy due to diagonal hh, hp, and pp interactions shown in Figs. 3(b)–3(f) and rearrangement interaction of the type 3(g). The effect owing to the UHF correction shown in Fig. 3(a) has already been taken account as described earlier. Numerical results with these additional modifications are given in Table IV for various interacting pairs. The values include the net sum of direct and exchange diagrams. In the second column, for the sake of comparison, we have listed the unmodified second-order contribution taken from Table II. The modified pair-correlation energies are obtained by using the energy denominator $D''_{pq;kk'}$ given in Eq. (16). All numerical values are again obtained by using states up to $l=5$ exactly, and the contribution from higher l states are estimated in the approximation described above. Our net pair-correlation energy is -0.20426 a.u. This is composed of 68% from the pair correlation among the L-shell electrons alone, followed by 23% from the K shell and 9% from the mixture. Additionally, about 4.4% of the total L-shell contribution of -0.13916 a.u. comes from excitations beyond $l=3$. A comparison of the individual pair-correlation energies with earlier CI results will be carried out in Sec. IV.

We will conclude the discussion on the pair-correlation energy by pointing out an important type of correlation which is characteristic of the open-shell atoms. We term it as the effect owing to "residue" diagrams. This corresponds to Figs. 2(b) and 2(c) plus the usual modifications of the types shown in 3(a)–3(g), when the participating hole states p and q are either $1s^-$ or $2s^-$ and one of the excited states is $2p^-$. These diagrams are found to

TABLE IV. Modified pair-correlation energies in a.u.

Pair (p, q)	Unmodified values[a]	Modified values[b]
$1s$, $1s$	−0.046 71	−0.047 70
$1s$, $2s$	−0.005 88	−0.005 87
$2s$, $2s$	−0.016 77	−0.013 80
$1s$, $2p$	−0.011 71	−0.011 53
$2s$, $2p$	−0.112 66	−0.078 56
$2p$, $2p$	−0.050 49	−0.046 80
Total	−0.244 22	−0.204 26

[a] Second-order pair-correlation energy.

[b] Includes correction due to higher-order diagrams as discussed in the text.

contribute about 29% of the total correlation energy. Additionally, the dominant contribution to this class of diagrams comes from the excitations $(2s^-, 2p) \to (2p^-, kd)$, which is about 63% of the $2s$-$2p$ correlation energy. This demonstrates that the contributions arising from the excited states (or unoccupied orbitals in CI terminology) which are nearly degenerate with unexcited RHF orbitals are very important. Obviously, these effects are not present for truly closed-shell systems such as the neon atom in the ^1S state. The sum of the residue and ECP diagrams may be identified with the orbital correlation energy in the calculation by Platas and Schaefer. This will be discussed in Sec. IV.

C. Pair-Pair Correlation

The numerical values for the pair-pair interaction diagrams in Fig. 4 are evaluated exactly using states up to $l = 5$ and are shown in Table V. However, since the ring diagrams, Figs. 4(d) and 4(e), are found to be important, their higher-order counterparts such as Fig. 4(h) and 4(i) are included in the approximation as described earlier. The net contribution from diagrams in Fig. 4 is found to be +0.011 37 a.u., which is 6% of the experimental correlation energy[21] of −0.1886 a.u., and is "opposite" in sign. This demonstrates that the pair-pair interactions cannot be neglected even in a relatively light atom such as nitrogen. The sum of ECP, pair, and pair-pair correlation energies in the present calculation is −0.195 92 a.u.

TABLE V. Contributions from the pair-pair correlation diagrams shown in Fig. 4.

Diagrams	Contribution (a.u.)
4(a)	0.000 99
4(b)	−0.002 55
4(c)	−0.003 83
Subtotal	−0.005 39
4(d)	0.008 30
4(e)	0.005 16
4(f)	0.001 65
4(g)	0.001 65
Subtotal	0.016 74[a]
Total	0.011 37

[a] Contributions from higher-order ring diagrams included as discussed in the text.

D. Many-Electron $(n > 2)$ Effects

Figures 5(a)–5(i) represent three-electron effects, whereas Figs. 5(j) and 5(k) describe four-electron effects. Inclusion of these effects in the CI approach will require use of trial wave functions including triple and quadruple excitations. The contributions from Fig. 5 are shown in Table VI. All possible diagrams with the same structure as those in Fig. 5 but with different arrangement of hole, particle lines, and exchange counterparts are included up to this order. Considerable numerical cancellations among these diagrams are observed in Table VI. The net three-electron contribution is +0.008 40 a.u., and the four-electron contribution is estimated to be −0.001 98 a.u.

IV. COMPARISON WITH THE EXPERIMENT AND EARLIER CALCULATION

Combining all the effects described so far, we arrive at our final value of −0.1895 a.u. We expect the result to be accurate to within ±0.003 a.u. This error is mainly from the neglect of nondiagonal terms in summing up the hp and pp interactions. The exact evaluation of these diagrams requires calculation of two-electron matrix elements involving at least three and four continuum states, which is prohibitively expensive in terms of the computer time.

A semiempirical estimate of the correlation energy is reported by Veillard and Clementi[21] to be −0.1886 a.u. This value is obtained by subtracting the corrections due to the relativistic effect and

TABLE VI. Contribution to the correlation energy from three- and four-electron effects (Fig. 5).

Description of Fig. 5 (Three-electron effect)	Contributions (a.u.)
a	0.001 28
b	0.005 81
c	−0.003 90
d	−0.001 02
e	−0.000 09
f	−0.000 22
g	0.004 41
h	0.002 44
i	−0.000 31
Subtotal	0.008 40
Four-electron effect	−0.001 98
Total	0.006 42

TABLE VII. Comparison of pair-correlation energies (a.u.) from the present work with those from Bethe-Goldstone calculation.

Pairs	Present work	Bethe-Goldstone[a] ($l \leq 3$)
Single excitation $e(p)$	−0.003 02	−0.003 194
$e(2p, 2p)$	−0.046 80	−0.029 869
$e(2p, 2s)$	−0.078 56	−0.083 439
$e(2s, 2s)$	−0.013 80	−0.013 633
L-shell total	−0.139 16	−0.126 941
$e(2p, 1s)$	−0.011 53	−0.008 679
$e(2s, 1s)$	−0.005 87	−0.005 337
KL-shell total	−0.017 40	−0.014 016
$e(1s, 1s)$, K shell	−0.047 70	−0.040 362
Total	−0.207 28	−0.184 512

[a] Reference 11.

Lamb shift from the experimental total energy evaluated by summing the individual ionization potentials. The error is quoted to be within 5%.

Extensive calculations have been performed by Nesbet on all first-row atoms using the Bethe-Goldstone approach.[11] In these calculations, the correlation energy E_c is obtained by summing the contribution due to the single excitations $e(p)$ and the independent pair-correlation energies $e(p, q)$ calculated variationally by replacing successively two spin orbitals of the single determinant HF function, without imposing the L^2 and S^2 symmetry restrictions. Thus, in the present case, the correlation energy is given by

$$E_c = \sum_p e(p) + \sum_{p,q} e(p, q) .$$

The comparison between our result and that of Nesbet is carried out in Table VII. The results in the present work for individual pair-correlation energies are listed in the second column, whereas those obtained by Nesbet are listed in the third column. The latter results were obtained by using Slater-type orbitals including orbitals of angular symmetry up to $l = 3$.

It is seen that the individual contributions from these two calculations are in over-all agreement with each other except in the case of $e(2p, 2p)$. The discrepancy between our $e(2p, 2p)$ and that of Nesbet cannot be explained by the contributions from higher l excitations. As seen from Table III, the main contribution to $e(2p, 2p)$ comes from the excited p and d orbitals. We think that more flexible radial functions for those excited-spin orbitals in CI calculation may reduce the existing discrepancy. Our net pair-correlation energy is seen to overshoot the experimental value by 10%. The same tendency was observed in the case of the atomic neon where the sum of pair-correlation energies gave 110% of the experiment. This fact shows that the individually computed pair-correlation energies are not additive. This point has been discussed at various places in the recent literature.[4,6–10] It is observed that the difference between the values for $e(2p, 2p)$ obtained by Nesbet and the present work, and the contributions from $l > 3$ to all pair-correlation energy diagrams except $e(2p, 2p)$, namely, −0.005 03 a.u. obtained by us, add up to −0.021 96 a.u. This is nearly equal to the difference between the net pair-correlation energies obtained by Nesbet and the present work. It will be interesting to see whether the use of more extended and flexible trail wave functions in his type of calculation will lead to the overestimate of the

TABLE VIII. Orbital correlation energies. Table is based on contributions from residue and ECP diagrams as discussed in the text.

Orbital excitation in SAPCI[a]	Orbital occupancy	Corresponding excitations in MBPT	Contribution (a.u.)	
			SAPCI	MBPT
$1s \rightarrow s_i$	$1s\, s_i 2s^2 2p^3$	$1s \rightarrow k_s$ (ECP) and $(1s^-, 2p^+) \rightarrow (2p^-, k_s^+)$	−0.000 26	−0.000 25
$1s \rightarrow d_i$	$1s\, d_i 2s^2 2p^3$	$(1s^-, 2p^+) \rightarrow (2p^-, k_d^+)$	−0.000 64	−0.000 63
$2s \rightarrow s_i$	$1s^2 2s\, s_i 2p^3$	$2s \rightarrow k_s$ (ECP) and $(2s^-, 2p^+) \rightarrow (2p^-, k_s^+)$	−0.004 52	−0.003 98
$2s \rightarrow d_i$	$1s^2 2s\, d_i 2p^3$	$(2s^-, 2p^+) \rightarrow (2p^-, k_d^+)$	−0.046 29	−0.049 60
$1s^2 \rightarrow 2p, p_i$	$2s^2 2p^4 p_i$	$(1s^-, 1s^+) \rightarrow (2p^-, k_p^+)$	−0.000 92	−0.000 92
$1s2s \rightarrow 2p, p_i$	$1s2s2p^4 p_i$	$(1s^-, 2s^\pm) \rightarrow (2p^-, k_p^\pm)$	−0.001 29	−0.000 25
$2s^2 \rightarrow 2p, p_i$	$1s^2 2p^4 p_i$	$(2s^-, 2s^+) \rightarrow (2p^-, k_p^+)$	−0.003 18	−0.002 62
		Total	−0.057 10	−0.058 25

[a] Reference 12.

correlation energy in the case of nitrogen, which is evidenced in the present work.

The overestimate of the correlation energy in the present work is remedied by the inclusion of the pair-pair interaction and many-electron effect. The sign of these contributions is positive as opposed to that of the pair-correlation energy, as explicitly demonstrated in Tables V and VI.

Platas and Schaefer have recently carried out a symmetry-adapted pair configuration-interaction calculation (SAPCI) on the nitrogen atom,[12] using a basis of 1633 configurations constructed from 19 530 Slater determinants including orbitals up to $l = 3$. Their value is − 0.183 15 a.u. Unfortunately, their individual pair-correlation results are not directly comparable to those from our diagrams, since their pair-correlation theory is based upon configurations. However, their orbital-correlation results can be identified in our calculation. They correspond to the ECP and residue diagrams discussed in Sec. III. The contributions from such effects are given in Table VIII and compared with the orbital correlation obtained by Platas and Schaefer. Following these authors' notation, we have listed the orbital excitations and the orbital occupancy in the first and second columns, respectively. In the third column, they are identified with the single- and double-excitation residue diagrams in the diagrammatic language. In agreement with their conclusion, we find that most (26%) of the orbital-correlation energy arises from $2s \rightarrow d_t$ excitation. Our total orbital-correlation energy is − 0.058 25 a.u., as compared with their value of − 0.057 10 a.u.

V. SUMMARY AND CONCLUSION

The many-body perturbation theory is seen to yield an accurate value of the correlation energy in the atomic nitrogen in its ground ^4S state. A useful result of the present work is a clear picture of the different effects which contribute to the correlation energy of open-shell systems. This is demonstrated in Table IX, where we have summarized our important conclusions. In the first column, we list the physical effects, followed by their numerical values obtained by appropriately regrouping the contributions from respective diagrams given earlier. The relative importance of these various effects is given in the third column in terms of percentages computed with respect to the experiment. All entries include explicitly contributions up to $l = 5$ states, while those from $l > 5$ are calculated by using a hydrogenic approximation of continuum wave functions. We find that the net correlation energy obtained by summing the contributions from the ECP and individual pairs [21 pairs for $N\,(^4S)$] is 110% of the experiment. This is composed of 79% from the pair correlation out of which 3.2% arises from states $l > 3$. About 31% of the contribution comes from the orbital-correlation energies. The pair-pair interaction amounts to 6%, whereas the many-electron effect is found to be 3.4%, which is quite significant. The contributions from the last two effects are opposite in sign as compared to the pair-correlation energy. It is also evident that the latter effects could not be neglected, if correlation energies of high accuracy are desired.

TABLE IX. Summary of results obtained in the present calculation.

Description	Contribution (a.u.)	Percentage[a] (%)
ECP	− 0.003 02	1.6
Residue diagrams	− 0.055 23[b]	29.3
Subtotal (orbital correlation energy)	− 0.058 25	30.9
Pair-correlation energy		
Contribution from $l \leq 3$	− 0.142 93	75.8
Contribution from $l > 3$	− 0.006 10	3.2
Subtotal (pair correlation)	− 0.149 03[b]	79.0
Net pair-correlation energy	− 0.207 28	109.9
Pair-pair correlation	+ 0.011 37	− 6.0
Many-electron effect	+ 0.006 42	− 3.4
Total correlation energy	− 0.18949 ± 0.003	
Experiment	− 0.1886 ± 0.0094	

[a] Computed with respect to the experiment.

[b] The sum of residue diagrams and pair correlation in this table adds up to − 0.204 26 a.u. as given in Table IV.

The advantage of the present method is that it utilizes a complete set of states in a perturbative treatment of atomic problems. The same basis set which is used here was already employed to study the hyperfine structure of the same atom. Additionally, we have very recently made use of the same complete set to study the electronic structure of NH_n-type molecules.[22] These will be presented in future publications.

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Correlation Energies of Ten-Electron Molecular Systems by a United-Atom Many-Body Perturbation Procedure: H_2O, NH_3, and CH_4[†]

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The linked-cluster many-body perturbation theory has been applied to the calculation of the correlation energies of the molecular systems H_2O, NH_3, and CH_4. The Hartree-Fock and correlation energies are obtained separately by combining the contributions from the pertinent diagrams. The calculated Hartree-Fock energies are in satisfactory agreement with the best previous theoretical results. The correlation energies (in a.u.) that we have obtained are −0.338, −0.317, and −0.312 for H_2O, NH_3, and CH_4, respectively. These latter energies are utilized for two purposes. One is to combine them with the total Hartree-Fock energies to obtain the total energies to compare with experiment. Secondly, they are subtracted from the "experimental" total energies to obtain reference Hartree-Fock energies with which to compare the energies from theoretical one-electron calculations.

I. INTRODUCTION

Recently, with advances in computing techniques, accurate variational molecular orbitals approximated as a linear combination of atomic orbitals (LCAOMO) wave functions approaching self-consistent Hartree-Fock character have become available in a number of diatomic molecules.[1] Correlation effects have also been included by variational techniques, using the configuration-interaction (CI) approach.[2] Corresponding calculations in polyatomic molecules involving three, four, and five atoms are much more time consuming, hence relatively few such molecules have been investigated for both HF and correlated wave functions and energies.

In recent work,[3] we have applied the linked-cluster many-body perturbation-theory (LCMBPT) procedure, which has been very successful for properties of atomic systems, to calculate the energy of hydrogen fluoride molecule using as a basis set the eigenfunctions of the corresponding united atom, namely, neon. The result for the energy obtained there agrees very well with experiment and the most detailed CI calculation available.[2] The result of the hydrogen fluoride work indicates that the many-body perturbation approach is certainly comparable in accuracy to the variational two-center method and involves a comparable amount of computational effort. The effort involved in calculating two-center integrals in the latter procedure is substituted by that for calculating