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Application of symmetry-adapted pair functions in atomic structure calculations: A variational-perturbation treatment of the Ne atom

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The atomic N-electron wave function of the independent-pair approximation is defined in terms of orbital configurations of one-electron functions and symmetry-adapted pair functions in the form of partial-wave (PW) expansions. This form is convenient for an extensive use of irreducible tensor operators. The formulation was used to set up a variational-perturbation scheme for closed-shell atoms in the case of the Rayleigh-Schrödinger perturbation theory with the symmetric sum of Hartree-Fock operators for the zeroth-order Hamiltonian (RS-HFPT). A detailed study of the second- and third-order correlation energies of Ne is made in order to analyze the nature of various correlation effects. All PW's up to $l',l'' \leq 9$ are considered. Particular attention is given to the problem of eliminating the radial basis saturation errors. The upper bound to the second-order energy is determined by means of 13 880 nonoptimized configurations to be -0.38638 a.u., which represents 99.3% of the "experimental" correlation energy. Extrapolation of the pair energies for l', $l'' > 9$ results in a second-order energy of -0.3879 a.u. (99.7% of the total correlation energy). The PW expansions for the $(ns,n's)$ pairs are compared for He, Be, and Ne. Remarkable regularities are observed, indicating that the PW formulation represents a convenient tool for the investigations of correlation effects. The third-order energy obtained for a shorter expansion of the first-order wave function amounts to 0.002 45 a.u. A discussion of the relative importance of the diagonal and off-diagonal contributions is presented, and detailed comparisons with the results of many other methods are made. It turned out that the RS-HFPT approach in the present formulation has several advantages over other perturbation methods.

I. INTRODUCTION

The problem of finding systematic ways to improve the independent-particle description by means of *ab initio* methods has been of interest to atomic physics for some time. There have been numerous attempts to obtain atomic energies based on wave functions in which correlation of electron motion is permitted. The procedure most frequently applied at the present time can be classified broadly under two categories: perturbation and variational types. An analysis of the newest *ab initio* methods of taking into account correlation effects seems to disclose the general trend of making use of perturbation theory. As has been noted by Dykstra *et al.*,[1] the actual distinction between many of the various correlation energy methods seems to be whether to use higher-order perturbation theory or to use first- or second-order perturbation theory in an interative manner to achieve a variational result. The ample variety of perturbational methods being applied in the many-electron theory makes it impossible for us to present a brief review. Among the review papers concerning this type of methods, those of Sinanoğlu,[2] Musher,[3] Kelly,[4] and Pople *et al.*[5] are very informative.

The perturbation approach seems to be well suited for describing correlation effects in many-electron systems. This is mainly due to the fact that it allows in the most natural way for decompositions of the global correlation effects into various elementary contributions. A perturbation theoretical description was used in the pioneering paper by Sinanoğlu[6] for demonstrating that correlation effects can be described in terms of independently determined pair functions.

The approach of Sinanoğlu is, of course, one of many formulations which have been or could be applied to the analysis of correlation effects. The means of description, the use of language, as well as the quantities obtained strongly depend on the formulation of the perturbation approach. This fact often impedes the analysis of the applicability of an individual formulation and makes it impossible to conclude on the numerical accuracy of the results obtained. It is not our purpose to classify the perturbation methods. We only indicate shortly the main factors which may be used to set up a classification.

Most of the working methods are based either on the Rayleigh Schrödinger (RS) of the Brillouin-Wigner methods of constructing the perturbation series. The former is the most commonly used in the many-electron theory. The main feature of each method is the choice of the unperturbed (zeroth-order) problem, which may consist either of an explicit partition of the Hamiltonian operator or of a partition of the matrix of the perturbed Hamiltonian.[7] Most of the recent methods are

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based on the use of zeroth-order Hamiltonians which are either Hartree-Fock (HF) Hamiltonians H_{HF} or are obtained from the latter by modifying the potential using, for example, the V^{N-1} form.[4] The choice of the HF problem as the starting point for a perturbation technique seems to be justified by the fact that the most commonly used definitions of correlation effects refer just to the HF energy and wave function. In such a formulation all perturbation corrections describe correlation effects. However, several ways of formulating the HF approximation for atomic systems, e.g., restricted-HF (RHF and unrestricted-HF (UHF) methods, which causes additional increase of the variety of perturbation methods mentioned above.

The next important feature of each perturbation theory is determined by the computational procedure used to obtain the corrections to the wave functions and eigenvalues. The methods based on the direct evaluation of the correcting terms have especially received much attention. Among these techniques various versions of the diagrammatic many-body methods[4, 8, 9] seem to play the most important role. The diagrams not only offer a pictorial description of correlation effects but also give rise to efficient algorithms for the numerical determination of terms in the many-body expansion. Another important class of perturbation techniques represent all variational-perturbation (VP) methods.[10] They are distinguished by the fact that they allow us to obtain upper bounds to the energy corrections of even order. The variational character of these techniques causes their results to be considered the most reliable, and may be used as reference points for the results of other methods.

These few remarks allow us to visualize the multitude of perturbation methods that may be set up to handle the correlation problem. Two questions arise immediately. How should one possibly compare all these methods to pick out the most effective ones that could be recommended for a general use? Are there any indications which of the existing classes of methods are best suited for the description of electron correlation effects in atoms?

Going back to the first question, one should admit that several attempts at finding general relations between different classes of approximation techniques exist.[11] However, conclusive arguments concerning the applicability of existing theoretical methods are provided only by test calculations of properties of real many-electron systems.

During the five decades of development in atomic structure calculations there have always been atoms that have served as standard test systems for the theoretical methods. The He atom indivisibly played this role for the first 30 years. In the early 1960's beryllium started its career. Now, at the end of the 1970's the state of computer technique seems to promote neon to the status of a standard test system for all advanced methods. Neon is in fact a rather interesting system for the analysis of correlation effects. It is complicated enough (with three shells) to allow one to make definite conclusions about the relative magnitude of different intrashell and intershell effects. Furthermore, Ne is the simplest closed-shell system containing electrons described by not totally symmetric atomic orbitals (p orbitals). The details of correlation effects within the p shell are still not so well understood as for the s shells. It may be interesting to note that properties calculated for the neon atom are often discussed jointly with their counterparts for small molecular systems.[5, 8, 12] Results obtained for Ne are commonly used for a general discussion of the relative importance of various kinds of contributions to the correlation energy, as e.g., the pair-pair interactions, the particle-particle and hole-hole ladder diagram contributions, etc. However, based on the numerical experience gained so far, one may arrive at the conclusion that within the class of RS perturbation theories (PT) the techniques based on the zeroth-order Hamiltonians in the HF form (RS-HFPT) are especially well suited for the description of correlation effects. Although, it is true that the choice of $H_0 = H_{HF}$ does not necessarily lead to the most rapid convergence of the whole perturbation series for the energy,[3, 13] such a formulation allows us to get the largest portion of correlation energy in the sum of the first two energy correction terms. It has also been found[14] that the RS-HFPT is invariant to mixing of degenerate orbitals and has the correct dependence on the number of particles. In turn, for diagrammatic approaches the choice $H_0 = H_{HF}$ results in a significant reduction of the number of contributing diagrams. An additional argument for the extensive use of the RS-HFPT is the fact that the accuracy of the correlation energy is about 100 times greater than the accuracy of the HF energies used in the calculations. This enables one to use a smaller basis set for the computation of the Hartree-Fock Roothaan orbitals without significant loss of accuracy. In turn, this possibility extends the range of applicability of these methods to quite a large systems, e.g., the present authors have recently reported second-order energies for the Zn^{2+} ion containing the $3d^{10}$ configurations.[15] For general nonclosed-shell atomic states there are several HF procedures. However, the single-configurational restricted Hartree-Fock orbitals are the most easily available in the literature[16] and for this reason they are preferred as the starting point for the electron correlation theories.

The main objective of this work is to obtain very accurate second-order energy (E_2) for the Ne within the framework of the VP method based on the RHF zeroth-order problem. As has been indicated above results of the RS-HFPT obtained within the framework of the VP technique may serve as reference points in the discussion of the relative merits of different formulations of the perturbation method. Several reliable VP results for the second-order energy of He and Be exist.[17-20] However, only Pan and King[20] have obtained such results for the Ne atom. These authors disclosed significant differences between their pair-correlation energies and the results obtained by Lee, Dutta, and Das[21] by means of the linked-cluster many-body perturbation theory. Pan and King admitted that the nature of the discrepancies is obscure and that the problem requires further study.

There are several other results obtained for Ne that need to be analyzed. We mention only the E_2 value of Barr and Davidson[7] which represents 121% (when extrapolated, 132%) of the "experimental" correlation energy. The latter result is by some authors (see e.g., Musher[3]) considered to be the best calculated E_2. Bearing in mind the above-mentioned fact that the neon results are commonly used to form a judgment about elementary correlation effects, one should aim towards improving the accuracy of the existing results for this system.

The main motivation for performing the present extensive computations was to obtain an accurate second-order energy for Ne using our formulation based on the use of "Symmetry-adapted pair-functions" of (SAPF) in a partial-wave (PW) form, and to elucidate the cause of the differences just mentioned. This seems to be possible because the results of our piloting calculations indicate that our method is well suited for the description of correlation effects in Ne.[22] In the present work careful attention is paid to computational accuracy.

Our second aim is to make a detailed identification of the contributions to E_2 from all types of electron pairs. Furthermore, we analyze the relative importance of various PW's. Results of the letter analysis are useful not only within the framework of perturbation theory, because it turns out that the angular structures of the perturbational and variational [configuration-interaction (CI)] wave functions are very much alike. Hence, one can apply our results as a guide when constructing accurate CI basis sets. We are also in a position to analyze the completeness of the basis sets used in various variational calculations, e.g., we indicate the reason why the CI-Hy method, when applied to Ne,[23] fails to yield accurate results.

Our third goal was to obtain some information about the magnitude of the third-order energy (E_3) for the Ne atom. The results reported so far have been obtained by means of less-accurate procedures. This rather low accuracy may be one of the reasons why the E_3 results of Pople *et al.*[5] and Urban *et al.*[8] differ in sign.

In order to secure our objects (especially the third goal) we set up a general technique for performing the calculations. The formulation is a little more general than required by the present variational-perturbation calculations. It may be useful in all formulations using the "independent pair approximations" (for definitions and references see Refs. 2 and 24–26). We define our approximate wave functions in terms of configurations (that are defined[25] as linear combinations of all determinants with specified nl values but with all possible m_l and m_s values for each orbital) and "symmetry-adapted pair functions," i.e., pair functions that are eigenfunctions of the two-particle L^2 and S^2 operators. The latter functions were introduced for the first time by Sinanoğlu in his many-electron theory.[6] Our approach aims toward a systematic use of the angular-momentum theory in the valuation of matrix elements of the Hamiltonian in the case of atomic configurations constructed from orbitals of higher angular momenta. It is in this case that elementary methods of evaluating matrix elements becomes impracticable. Recently, Sasaki[27] presented an irreducible tensor-operator method of finding matrix elements arising in the configuration-interaction method. Since in our approach to the independent pair approximation the wave functions are set up using elementary functions (spin orbitals and SAPFs) that have a definite tensor operator character, we can make extensive use of the simplifications provided by the application of the theory of angular momentum. The only formulation using a many-electron wave function of definite symmetry, comprising SPAF in a way convenient for the use of tensor-operator methods, may be found in the paper of Chisholm and Dalgarno[28] concerning the nuclear-charge-expansion method.

In Sec. II A we present the formulation of our approach to the independent pair approximation and present a more-detailed discussion for the most-simple closed-shell state.

Section II B contains an outline of our version of the VP approach which is presented in a form applicable to all closed-shell atomic systems. Some computational aspects are discussed in Sec. III. In Sec. IV we present our numerical results of the second-order correlation energy of Ne; we also extensively compare our results with those calculations. Finally, the E_3 results are presented in Sec. V.

II. METHODOLOGY

A. Symmetry-adapted wave function in the independent-pair approximation

We shall follow the standard approach of the independent-pair approximations introducing a reference state ϕ_0 that represents a fairly good approximation to the eigenfunction of the N-electron Schrödinger equation. ϕ_0 is usually taken in the orbital approximation with the same spin and angular-symmetry properties as the exact wave function. In most cases the reference function is taken in the single-configurational form, although, in case of quasidegeneracy a multiconfigurational function may be more suitable (see e.g., Ref. 13). For the sake of simplicity we confine ourselves in this paper to a single-configuration reference state.

Having specified ϕ_0, the approximate wave function of an N-electron system in the pair-correlation approximation may be written

$$\begin{aligned}\Psi(\alpha, L, S, M_L, M_S \mid 1, 2, \ldots, N) &= \phi_0(\alpha, L, S, M_L, M_S \mid 1, 2, \ldots, N)\\ &\quad + \chi(\alpha, L, S, M_L, M_S \mid 1, 2, \ldots, N) \qquad (1)\end{aligned}$$

where χ stands for the independent-pair correlation function. For our purpose, it is convenient to represent χ as a sum of wave functions describing intrashell (TRA) and intershell (TER) correlation effects

$$\begin{aligned}\chi(\alpha, L, S, M_L, M_S \mid 1, \ldots, N) &= \chi_{\mathrm{TRA}}(\alpha, L, S, M_L, M_S \mid 1, \ldots, N)\\ &\quad + \chi_{\mathrm{TER}}(\alpha, L, S, M_L, M_S \mid 1, \ldots, N)\,. \qquad (2)\end{aligned}$$

We use the LS-coupling scheme and assume that Ψ, ϕ_0, and χ are eigenfunctions of L^2, S^2, L_z, and S_z. The index α stands for any other quantum number needed to specify the state.

For compactness of notation the electron coordinates will be suppressed whenever misunderstanding is excluded. Moreover, we use the following shorthand notation for sets of quantum numbers:

$$\overline{T} \longleftrightarrow (L, S, M_L, M_S), \quad \overline{t} \longleftrightarrow (l, s, m_l, m_s)\,,$$

$$T \longleftrightarrow (L, S), \quad t \longleftrightarrow (l, s)\,,$$

$$\tilde{T} \longleftrightarrow (M_L, M_S), \quad \tilde{t} \longleftrightarrow (m_l, m_s)$$

In the new convention functions (1) and (2) can be written

$$\Psi(\alpha, \overline{T}) = \phi_0(\alpha, \overline{T}) + \chi(\alpha, \overline{T})\,, \qquad (1a)$$

$$\chi(\alpha, \overline{T}) = \chi_{\mathrm{TRA}}(\alpha, \overline{T}) + \chi_{\mathrm{TER}}(\alpha, \overline{T})\,. \qquad (2a)$$

Let us now proceed to the details of constructing the functions involved.

1. Reference function

To construct the N-electron wave function ϕ_0 of an atom comprising p groups of equivalent electrons (subshells) identified by the pair of quantum numbers $n_i l_i$, we start from antisymmetrized wave functions of the various subshells. We prescribe the variables of the N_i electrons of the ith subshell to be ordered in the sequence of increasing values of the electron index. We indicate the wave function of this subshell,[30] constructed by LS coupling, by $|\, l_i^{N_i}(\alpha_i, T_i)]$, where l_i stands for the pair of quantum numbers $n_i l_i$.

The antisymmetric wave function $\Psi_0(\alpha, \overline{T})$ of the whole atom in the orbital approximation can be written

$$\Psi_0(\alpha, \overline{T}) = \hat{\mathfrak{A}} \Lambda_0(\alpha, \overline{T})\,, \qquad (3a)$$

where $\hat{\mathfrak{A}}$ is an antisymmetrizer for the whole system that antisymmetrizes with respect to permutations involving interchanges of electrons between the subshells (see, e.g., Refs. 29 and 30). Λ_0 is an unsymmetrized wave function of the whole N-electron atom constructed by multiplying the subshell functions $|\, l_i^{N_i}(\alpha_i, T_i)]$ and adding their angular momenta $L_i S_i$ according to some prescription indicated by A_q to resultant L and S. We indicate this wave function by

$$\Lambda_0(\alpha, \overline{T}) = |\, l_1^{N_1}(\alpha_1, T_1) \cdots l_r^{N_r}(\alpha_r, T_r); \{T_T\}; \tilde{\alpha}, \overline{T}]\,, \qquad (3b)$$

where $\{T_T\}$ represents the set of quantum numbers describing the intermediate momenta arising in the process of coupling the momenta $T_1, T_2, \ldots, T_r$ of the individual shells. $\tilde{\alpha}$ is obtained from α by neglecting the set $\{T_T\}$.

More explicitly $\Lambda_0(\alpha, \overline{T})$ may be written

$$\begin{aligned}\Lambda_0(\alpha, \overline{T}) &= \sum_{\{\tilde{T}\}} \begin{bmatrix} T_1 \cdots T_r T \\ \tilde{T}_1 \cdots T_r \tilde{T} \end{bmatrix}^{A_q}_{\{T_T\}}\\ &\quad \times |\, l_1^{N_1}(\alpha_1, \overline{T}_1)] \cdots |\, l_r^{N_r}(\alpha_r, \overline{T}_r)]\,, \qquad (3c)\end{aligned}$$

where

$$\begin{bmatrix} T_1 \cdots T_r T \\ \bar{T}_1 \cdots \bar{T}_r \bar{T} \end{bmatrix}^{A_q}_{\{T_T\}}$$

denotes the generalized Clebsch-Gordan coefficient,[29] which may be represented by proper sums of product of ordinary Clebsch-Gordan (CG) coefficients. The sum is to be taken over quantum numbers of the intermediate momenta. The superscript A_q indicates the coupling format of the angular momenta involved.[29] The most conventional coupling format A_0 assumes that angular momenta of the subshells are added consecutively.[29]

2. Intrashell correlation function

The intrashell contribution χ_{TRA} is defined as a sum of contributions from individual subshells ($1s,2s,2p,3s,\ldots$,etc.) indicated by the index i,

$$\chi_{\mathrm{TRA}}(\alpha,\overline{T})=\sum_i \chi^i_{\mathrm{TRA}}(\alpha,\overline{T}) , \tag{4a}$$

with

$$\chi^i_{\mathrm{TRA}}(\alpha,\overline{T})=\hat{\mathfrak{A}}\Lambda^i_{\mathrm{TRA}}(\alpha,\overline{T}) , \tag{4b}$$

$$\Lambda^i_{\mathrm{TRA}}(\alpha,\overline{T})=\sum_{\alpha'_i T'_i}\sum_{T_p}(l_i^{N_i-2}(\alpha'_i,T'_i),\, l_i^2(T_p)\,|\}l_i^{N_i}(\alpha_i,T_i))$$

$$\times\,|\,l_1^{N_1}(\alpha_1,T_1),\ldots,\hat{\mathfrak{A}}^{(i)}[l_i^{N_i-2}(\alpha'_i,T_i),u_i(T_p);\alpha_i,T_i]\cdots l_r^{N_r}(\alpha_r,T_r);\{T_T\};\alpha\overline{T}] , \tag{4c}$$

where $u_i(T_p)$ stands for the SAPF inserted in place of an uncorrelated orbital pair function $|\,l_i^2(T_p)]$. The antisymmetrizer $\hat{\mathfrak{A}}^{(i)}$ performing antisymmetrization of the coupled product of wave functions of N-2 electrons and the pair function must be introduced to ensure that the part of Λ^i_{TRA} describing the ith subshell is antisymmetric. The symbol $(l^{N-2}(\alpha',T'),\,l^2(T_p)\,|\}l^N(\alpha,T))$ denotes the two-electron coefficients of fractional parentage[29] (tcfp), which are nonzero only for certain pairs of the T'_i and T_p sets of indices. This fact causes a considerable reduction of the number of terms in (4c). Let us note that the pair-correlation effects within a given shell are described so that the coupling scheme of the shells does not change.

3. Intershell correlation function

The intershell contribution $\chi_{\mathrm{TER}}(\alpha,T)$ is expressed as a sum over contributions from pairs of subshells

$$\chi_{\mathrm{TER}}(\alpha,\overline{T})=\sum_{i<j}\chi^{ij}_{\mathrm{TER}}(\alpha,\overline{T}) , \tag{5a}$$

where

$$\chi^{ij}_{\mathrm{TER}}(\alpha,\overline{T})=\hat{\mathfrak{A}}\Lambda^{ij}_{\mathrm{TER}}(\alpha,T) , \tag{5b}$$

with

$$\Lambda^{ij}_{\mathrm{TER}}(\alpha,T)=\sum_{\{T_W\}c\alpha'} M(T_1,\ldots,T_r;\{T_T\};\{T'_T\};T)$$

$$\times\Lambda'^{ij}_{\mathrm{TER}}(\alpha',\overline{T}) . \tag{5c}$$

In Eq. (5c), $M(T_1,\ldots,T_r;\{T_T\};\{T'_T\};T)$ denotes the recoupling coefficient from the coupling scheme of $\Lambda_0(\alpha,\overline{T})$, which is characterized by the set $\{T_T\}$, to a coupling scheme in which the resultant momenta of the $l_i^{N_i-1}$ and $l_j^{N_j-1}$ groups are coupled together and afterwards coupled to the resultant moments of the pair of electrons characterized by l_i and l_j. The result of this procedure is then coupled to the momenta of the other r-2 subshells. If the A_0 coupling format is taken in ϕ_0, the final coupling scheme in $\Lambda'^{ij}_{\mathrm{TER}}$ may be also chosen of the A_0 type for the changed ordering of the subshells caused by moving the second of the (i,j) pair of subshells to a position just behind the first. The set of quantum numbers describing the intermediate states in the new scheme is denoted by $\{T'_T\}$. The set $\{T_W\}$ represents all quantum numbers refering to intermediate angular momenta which had to be introduced when changing the coupling scheme.

For the applications considered in this paper $\Lambda'^{ij}_{\mathrm{TER}}$ may be defined as follows:

$$\Lambda'^{ij}_{\mathrm{TER}}(\alpha',\overline{T})=\sum_{\alpha'_i,T'_i}\sum_{\alpha'_j,T'_j}\sum_{T_{ij}}(l_i^{N_i-1}(\alpha'_i,T'_i),\,l_i\,|\}l_i^{N_i}(\alpha_i,T_i))(l_j^{N_j-1}(\alpha'_j,T'_j),\,l_j\,|\}l_j^{N_j}(\alpha_j,T_j))$$

$$\times\,|\,l_1^{N_1}(\alpha_1,T_1)\cdots\hat{\mathfrak{A}}_{ij}((l_i^{N_i-1}(\alpha'_i,T'_i)l_j^{N_j-1}(\alpha'_j,T'_j);T'_{ij}),u_{ij}(T_{ij});T''_{ij})\cdots l_r^{N_r}(\alpha_r,T_r);\{T'_T\};\alpha',\overline{T}] \tag{5d}$$

where $(l^{N-1}(\alpha',T'),\,l\,|\}l^N(\alpha,T))$ are one-electron coefficients of fractional parentage (cfp) and u_{ij} denotes the intershell SAPF. The intermediate angular-momentum quantum numbers T_{ij}, T'_{ij}, and T''_{ij} are included in the set $\{T_W\}$ of summation indices in Eq. (5c). In Eq. (5d) the values of (α'_i,T'_i) and (α'_j,T'_j) are limited to those that belong to nonzero cfp.

4. *Pair functions*

We have not specified the form of the SAPF's so far. In principle, any antisymmetric two-electron function that is symmetry adapted can be taken. For our purpose, it is convenient to define a general SAPF function by the equation

$$u_{ij}(\tilde{T}_{ij}\,|\,1,2)=\mathfrak{B}\sum_{ll}R^{ij,T_{ij}}_{l'l''}(r_1,r_2)\times Z^{(l',l'')}(L,M_L\,|\,\delta_1,\delta_2)\mathfrak{S}(S,M_S\,|\,\sigma_1,\sigma_2)\,, \tag{6a}$$

where in the case of intrashell pairs we take $i=j$ and $\overline{T}_{ij}=\overline{T}_p$. $\mathfrak{B}$ is a two-particle antisymmetrizer and $\mathfrak{S}(S,M_S\,|\,\sigma_1,\sigma_2)$ denotes the spin part of the SAPF. The function $Z^{(l'l'')}$ representing the angular part of the pair function may be written as a coupled product of spherical-tensor operators[29] $C^{(l)}_q(\delta_1)$,

$$Z^{(l'l'')}(L,M_L)=(4\pi)^{-1}[(2l'+1)(2l''+1)]^{1/2}\times[C^{(l')}(\delta_1)\times C^{(l'')}(\delta_2)]^{(L)}_{M_L}\,, \tag{6b}$$

where δ denotes the pair of angles (θ,φ). As a matter of fact, Eq. (6a) represents a Legendre expansion for the pair function. A special case of this expansion, for $l'=l''$, has been used in the discussion of two-electron problems by many authors, and has been often referred to as the "partial-wave expansion" (see, e.g., Ref. 17). We shall use this terminology also for the more general expansion (6a) which includes terms with $l'\neq l''$.

Definition (6a) represents the most general expression for pair functions. By a proper definition of the radial function $R^{ij,T_{ij}}_{l'l''}(r_1,r_2)$, all known pair functions may be obtained. If the radial functions depend on r_1 and r_2, Eq. (6a) depicts an CI-type pair function. On the other hand, if the radial functions depend also on the variables $r_<$ and $r_>$, which denotes the larger and smaller of the magnitudes of r_1 and r_2, respectively, Eq. (6a) explicitly defined correlated pair functions, i.e., functions depending explicitly on the interelectron distances.

5. *Application to closed-shell systems*

Let us consider an atomic system consisting of r closed subshells. Owing to the fact that (for all i) $\overline{T}_i=\overline{O}$ ($\overline{O}$ denotes that all quantum numbers of the given set are equal to zero), the formalism simplifies drastically.

For closed-shell systems we can rewrite Eq. (4c) as

$$\Lambda^{i}_{\mathrm{TRA}}(\overline{0})=\sum_{T_p}\Lambda^{i,T_p}_{\mathrm{TRA}}(\overline{0})\,, \tag{4d}$$

where

$$\Lambda^{i,T_p}_{\mathrm{TRA}}(\overline{0})=(l_i^{4l_i}(T_p),\;l_i^2(T_p)|\}\,l_i^{4l_i+2}(0))\,|l_1^{4l_1+2}(0)\cdots\hat{\mathfrak{A}}^{(i)}(l_i^{4l_i}(T_p),\,u_i(T_p)\,;0)\cdots l_r^{4l_r+2}(0);\{0\};\overline{0}]\,.$$

$\{\overline{0}\}$ denotes that all intermediate momenta are equal to zero.

The similar part of the interpair correlation function [Eq. (5d)] will assume the following form:

$$\Lambda'^{ij}_{\mathrm{TER}}(\overline{0})=\sum_{T_{ij}}\Lambda^{ij,T_{ij}}_{\mathrm{TER}}(\overline{0}), \tag{5e}$$

where

$$\Lambda^{ij,T_{ij}}_{\mathrm{TER}}(\overline{0})=\left(\frac{T_{ij}}{t_i,t_j}\right)^{1/2}|l_1^{4l_1+2}(0)\cdots\;\hat{\mathfrak{A}}_{ij}((l_i^{4l_i+1}(t_i),l_j^{4l_j+1}(t_j);T_{ij}),u_{ij}(T_{ij}):0)\cdots l_r^{4l_r+2}(0);\{0\};\overline{0}]\,.$$

$[a,b]$ is a shorthand notation of $(2a+1)(2b+1)$.

Similar to Eqs. (4b) and (5b) let us define

$$\chi^{i,T_p}_{\mathrm{TRA}}(\overline{0})=\hat{\mathfrak{A}}\Lambda^{i,T_p}_{\mathrm{TRA}} \tag{7a}$$

and

$$\chi^{ij,T_{ij}}_{\mathrm{TER}}(\overline{0})=\hat{\mathfrak{A}}\Lambda^{ij,T_{ij}}_{\mathrm{TER}}\,. \tag{7b}$$

Now, we can rewrite Eq. (2) in the more convenient form

$$\chi=\chi_{\mathrm{TRA}}+\chi_{\mathrm{TER}}=\sum_{i}\sum_{T_p}\chi^{i,T_p}_{\mathrm{TRA}}+\sum_{ij}\sum_{T_{ij}}\chi^{ij,T_{ij}}_{\mathrm{TER}}\,, \tag{8}$$

where we omit the symbol $\overline{0}$.

The calculation of matrix elements of one- and two-particle operators between wave functions of the general form discussed above is a very complicated problem. It may be performed by a similar methodology as in the case of configurations containing several open subshells. Several approaches to the latter problem exist.[29,30] The spin and angular dependence of the matrix elements is separated out being expressed in terms of n-j symbols and fractional parentage coefficients.

In the Appendix we consider the matrix elements used in our calculations of the second- and third-order energies for closed-shell systems if ϕ_0 is taken to be the restricted HF wave function. It has been shown by several authors[6,20] that for such a choice of the zeroth-order problem all pair functions are strongly orthogonal to the HF orbitals. This requirement is also imposed on our pair functions.

B. Variational-perturbation method for closed-shell atomic systems

Let us consider a closed-shell N-electron atom. We choose the unperturbed Hamiltonian in the HF form, i.e.,

$$H_0 = H_{\mathrm{HF}} = \sum_{i=1}^{N} h(i) . \tag{9a}$$

with $h(1)$ denoting the one-electron Fock operator

$$h(1) = t(1) + \sum_{k=1}^{N} V_k(1) , \tag{9b}$$

where

$$V_k(1) = (\varphi_k(2)|(1-P_{12})r_{12}^{-1}|\varphi_k(2))_{(2)} .$$

Here $t(1)$ denotes the bare-nucleus one-electron Hamiltonian, P_{12} indicates the two-particle permutation operator, φ_k are HF spin orbitals, and the subscript denotes integration over coordinate set 2. The perturbation operator is

$$H_1 = \sum_{i>j}^{N} r_{ij}^{-1} - \sum_{i=1}^{N}\sum_{k=1}^{N} V_k(i) . \tag{9c}$$

The first-order wave function Ψ_1 satisfies[10]

$$(H_0 - E_0)\Psi_1 + (H_1 - E_1)\Psi_0 = 0 ,$$

where E_0 and E_1 stand for the zeroth- and first-order energy, respectively. Within the variational-perturbation procedure Ψ_1 is approximated by the function χ minimizing the Hylleraas functional[10]

$$J_1[\chi] = \langle\chi|H_0 - E_0|\chi\rangle + 2\langle\chi|H_1 - E_1|\Psi_0\rangle , \tag{10}$$

within a given class of trial functions.

It has been shown by Sinanoğlu[6] that for closed-shell systems the first-order wave function may be represented as a sum of antisymmetrized products of occupied HF spin orbitals and pair functions which are strongly orthogonal to the latter. Hence, the variational function χ may be written in a from that differs from the exact function Ψ_1 in that it contains trial pair functions in place of the exact ones.

We employ symmetry-adapted pair functions as the building blocks of the N-electron first-order functions χ in a way that has been specified in Sec. II A, i.e., we write the function χ in the form specified by Eq. (8).

Inserting (8) in (10), and taking into account only the nonzero matrix elements of one- and two-electron operators listed in the Appendix, one gets further

$$J_1[\chi_1] = \sum_{i}\sum_{T_p} J_1[\chi_{\mathrm{TRA}}^{i,T_p}] + \sum_{i>j}\sum_{T_{ij}} J_1[\chi_{\mathrm{TER}}^{ij;T_{ij}}] . \tag{11}$$

This equation represents a decompositions of the Hylleraas functional (10) into a sum of functionals depending on the individual pair contributions. Hence, the problem of minimizing the functional (10) reduces to the independent minimizations of a set of Hylleraas functionals involving only one pair function each time.

To apply the variational-perturbation method we express the radial function in Eq. (6a) in terms of radial basis functions ρ_s,

$$R_{l'l''}^{ij;T_{ij}}(r_1, r_2) = \sum_{s} c_{sl'l''}^{ij;T_{ij}} \rho_s(r_1, r_2) . \tag{12}$$

Our radial basis functions are defined as

$$\rho_s(r_1, r_2) = R(u_s, \eta_s|r_1)R(t_s, \mu_s|r_2) , \tag{13a}$$

where

$$R(u\eta|r) = r^{u}\exp(-\eta r) . \tag{13b}$$

The linear coefficients $c_{sl'l''}^{ij;T_{ij}}$ are determined from the variational-perturbational procedure.

To ensure the strong orthogonality of the pair functions to the HF spin orbitals we apply the strong-orthogonality projection operator defined as

$$\hat{\Omega}(1,2) = \hat{\Omega}(1)\hat{\Omega}(2) , \tag{14}$$

with

$$\hat{\Omega}(i) = 1 - \sum_{k=1}^{N} |\varphi_k(i)][\varphi_k(i)| .$$

The strongly orthogonal approximate SAPF may finally be written in the form

$$u_{ij}(\overline{T}_{ij}|1,2) = \hat{\Omega}(1,2) \sum_{sl'l''} c_{sl'l''}^{ij;T_{ij}} \omega_{sl'l''}(\overline{T}_{ij}|1,2) , \tag{15}$$

where we use the PW basis functions

$$\omega_{sl'l''}(\overline{T}|1,2) = \hat{\mathfrak{B}}\rho_s(r_1, r_2)Z^{l'l''}(L, M_L|\delta_1, \delta_2) \times \mathfrak{S}(S, M_s|\sigma_1, \sigma_2) . \tag{16}$$

Minimization of the Hylleraas functionals lead us to the sets of equations

$$\sum_{sl'l''} c_{sl'l''}^{ij;T_{ij}} \{2[\Omega\omega_{sl'l''}(T_{ij})||h||\Omega\omega_{qm'm''}(T_{ij}) - (\epsilon_i + \epsilon_j)(\Omega\omega_{sl'l''}(T_{ij})|\Omega\omega_{qm'm''}(T_{ij}))\} + [l_i l_j(T_{ij})||r_{12}^{-1}||\Omega\omega_{qm'm''}(T_{ij})] = 0 \tag{17}$$

(s, l', l'' take values from the same set as $q, m'm''$). In (17) the symbol $[\| \|]$ denotes the reduced matrix element.[30] l_i stands for the RHF orbital of the ith shell, and ϵ_i is the respective orbital energy. $|l_i l_j(\bar{T}_{ij}))$ denotes the normalized pair function of definite symmetry $\bar{T}_{ij}$ setup of HF spin orbitals.

Let us note that Eq. (17) does not depend on the M_L and M_S quantum numbers of the pair function.

It may be seen from Eq. (17) that we have performed a direct reduction of the N-electron problem to a two-electron problem. Our way of reduction differs from the method commonly employed[6,18-20] in that it uses SAPF in place of spin-orbital pairs from the very beginning. Furthermore, we do not use as an intermediate step the explicit equations for the first-order spin-orbital pair functions. As a matter of fact, these equations are of no practical importance in the VP approach. This is due to the fact that one has to consider a great number of them (see, e.g., Ref. 18), and that their handling by the variational-perturbation method requires imposing additional constraints on the trial functions. Therefore, eventually one is forced to transform these pair equations and to proceed to equations for the pair functions of definite symmetry (see, e.g., Ref. 20) which, in turn, would allow us to obtain Eq. (17).

It may be worthwhile to mention that Shibuya and Sinanoğlu[32] developed another method for reducing the equations for the first-order wave function of an N-electron system into equations for the radial parts of the pair functions for closed-shell systems. The method is based on the application of the symmetric group S_N. These authors presented also a generalization to the open-shell case.[32]

For pair functions defined as in Eq. (16), one can prove that the two-matrix elements in the curly brackets vanish, unless the pairs $l'l''$ and $m'm''$ are equal. This involves a reduction of the sets of linear equations for each pair to sets of equations determined by fixed values of l' and l'', i.e., by a given partial wave. Let us make the observation, that due to the indempotency of $\hat{\Omega}$, i.e., $\hat{\Omega}^2 = \hat{\Omega}$, and to the fact that $\hat{\Omega}\hat{h} - \hat{h}\hat{\Omega} = 0$, one can omit one projection operator in the first two matrix elements of Eq. (17). Let A denote the set of indices specifying a partial wave $l'l''$ of the pair determined for electrons of the shells i and j with a symmetry specification T_{ij}, i.e.,

$$A \leftarrow (l', l'', i, j, T_{ij}) \,. \tag{18}$$

We can finally write the sets of equations in the matrix form

$$C^{(A)\dagger} W^{(A)} + V^{(A)} = 0 \,, \tag{19}$$

where $C^{(A)}$ stands for the column matrix of linear coefficients. The $W^{(A)}$ and $V^{(A)}$ matrices are defined by

$$\begin{aligned} W_{sq}^{(A)} &= 2[\omega_{sl'l''}(T_{ij}) \| h \| \hat{\Omega}\omega_{ql'l''}(T_{ij})] \\ &\quad - (\epsilon_i + \epsilon_j)(\omega_{sl'l''}(T_{ij}) | \Omega\omega_{ql'l''}(T_{ij})) \,, \\ V_q^{(A)} &= [l_i l_j(T_{ij}) \| r_{12}^{-1} \| \Omega\omega_{ql'l''}(T_{ij})] \,. \end{aligned} \tag{20}$$

Thus, we see that the VP approach allows for a reduction of the system of linear equations for all linear coefficients $C_{sl'l''}^{ijT_{ij}}$ of the first-order function to independent systems of equations of form (19) for every PW of each SAPF, i.e., for the indices i, j, T_{ij}, l', and l'' fixed. This possibility of decoupling the N-electron problem into sets of independent problems for individual pairs constitute the most attractive feature of the second-order perturbation method.

The form of the $\omega_{sl'l''}$ basis function makes it possible to express the matrix elements in Eq. (19) in terms of elementary radial integrals involving the $\rho_s(r_1, r_2)$ functions. These integrals need to be generated only once. There are several simplifications inherent in the form of Eq. (19). For a fixed radial function basis set some subsidiary matrices may be used many times, e.g., let us note that the two-matrix elements entering $W_{sq}^{(A)}$ depend only on the PW and symmetry of the pair functions. They do not depend on the quantities specifying a pair.

Once the $C^{(A)}$ matrices are determined, the approximation to the second-order energy (E_2) can be readily obtained as the value of the Hylleraas functional.[10] Hence, we can express E_2 in terms of increments $E^{(2)}(A)$ obtained for a given set A of the PW and pair-function indices, i.e.,

$$E_2 = \sum_{(A)} g(A) E^{(2)}(A) \,, \tag{21}$$

where[10]

$$E^{(2)}(A) = \underline{C}^{(A)\dagger} \underline{V}^{(A)} \tag{22}$$

and $g(A) = g(T) = (2L+1)(2S+1)$ represents the number of possible pairs for given L and S. One can further define the second-order pair energy for the pair of symmetry T belonging to the shells i and j as

$$E_{ij}(T) = \sum_{l'l''} E^{(2)}(l', l'', i, j, T) \,. \tag{23}$$

we can express E_2 in terms of second-order pair energies as

$$E_2 = \sum_{i,j} \sum_{T} g(T) E_{ij}(T) \,. \tag{24}$$

III. DETAILS OF THE CALCULATIONS

Our approach is based on the unperturbed Hamiltonian in the restricted HF form. In the present calculation for the Ne atom we have used the accurate analytical HF orbitals of Clementi and Roetti[16] spanned by Slater-type orbitals. The linear coefficients of the HF orbitals are slightly modified to fulfill the orthonormalization conditions with double-precision accuracy. Since it has been demonstrated by several authors (see, e.g., Refs. 18 and 20) that the error in the self-consistent-field (SCF) energy is about a hundred times greater than the error in the correlation energy, we may assume that at least the first five significant figures of our energy increments are not affected by the approximate character of the HF orbitals.

The sets of linear equations (19) have been solved for all symmetry adapted pairs of Ne. All PW's for which $l', l'' \leqslant 9$ have been explicitly considered. The contributions for $l', l'' > 9$ have been estimated.

Special attention has been paid to the problem of completeness of the radial basis set defined by Eq. (13a). We have used several radial bases defined by various sets of nonlinear parameters obtained by largely *ad hoc* procedures designed to completely span the expansion space of the basis. For reasons that will be clear later, much work has been invested to set up basis sets allowing minimization of the $l' = l'' = 1$ and $l' = l'' = 2$ PW increments for the pairs of the $2p$ shell. However, for a 120-dimensional problem almost all bases led to vary similar results. Only the $1s^2$ pair energy and some PW contributions with high l' and l'' indices disclosed some dependence on the choice of the basis set. Our computational experience allows us to believe that the first four significant figures of the second-order energy reported below are not affected by the residual incompleteness of the radial basis set used.

The most important contributions to the correlation energies (i.e., the PW results for $l', l'' \leqslant 4$) have been obtained using the radial basis (13a) set up by taking all possible products of the $R(u, \eta \mid r)$ functions with the parameters specified in Table I. This function have been obtained by complementing the function set used by Nesbet[33] in his Ne calculations. From the 20 basis functions listed in Table I we obtained 210 two-electron radial basis functions. This set represents a well-balanced set for PW's with indices $l', l'' \leqslant 4$. For all PW's of the $1s^2$ pair and for the higher PW's of all other pairs other partially optimized radial basis sets have been employed. For these functions several sets of subsidiary integrals were generated and stored. In each calculation 120 (for $l' = l''$), or 130 (for $l' \neq l''$) functions have been used. For the lower PW's ($l', l'' \leqslant 4$) these functions have been selected out of the 210 function set according to the rule that an increase of the $l'l''$ indices of the PW enlarges the participation of functions containing higher powers of r.

TABLE I. Parameters of the functions $R(u, \eta \mid r)$.

No.	u	η	No.	u	η
1	0	2.0	11	2	4.214[a]
2	0	4.0	12	2	10.0
3	0	8.9141[a]	13	2	21.63[a]
4	0	12.3545[a]	14	3	4.214[a]
5	0	21.63	15	3	10.0
6	1	2.1839[a]	16	3	21.63[a]
7	1	3.4921[a]	17	4	4.214
8	1	5.5	18	4	8.0
9	1	11.0	19	4	21.63[a]
10	1	21.63[a]	20	5	21.63

[a] Used for the construction of the Nesbet (Ref. 33) basis.

Special care has been paid to avoid linear dependences in the set. To supervise the numerical stability of the results for each partial wave, Eq. (19) has been also solved for some purposely chosen subsets of the final basis sets.

Our final first-order wave functions for Ne consists of 13 880 nonoptimized configurations constructed from about 300 000 distinct Slater determinants. This basis may be compared with its counterpart used in the most extensive CI calculation which contained 1571 configurations. A general computer program applicable to all closed-shell atomic system has been developed. The computations were carred out on an IBM 370/145 computer in double precision arithmetics.

IV. SECOND-ORDER ENERGY RESULTS AND DISCUSSION

A. Partial-wave increments to the pair-correlation energies

We have solved Eq. (19) and calculated the PW increments to the second-order energy $E^{(2)}(A)$. The results are presented in Tables II–V. For reasons of convenience we use the more-explicit spectroscopic way of designing electron pairs, e.g., we write $1s2p(^1P)$ to indicate the intershell pair (involving the $1s$ and $2p$ shells) corresponding to $L = 1$ and $S = 0$. We also prefer to use the letter convention for the designation of PW's, i.e., we use $s, p, d, f, \ldots$ to denote $l = 0, 1, 2, 3, \ldots$, respectively. For example, *dd* denotes the PW designated by $l' = l'' = 2$.

Table II lists the results for the four $(ns, n's)$ pairs. It is apparent that the relative importance of various PW contributions is different for each pair. For the $1s^2(^1S)$ and $1s2s(^3S)$ pairs, the *pp* wave provides the dominating contribution. For

TABLE II. Partial-wave contributions $E^{(2)}(A)$ and pair energies for the $(ns, n's)$-pairs.[a]

Partial-wave contributions	Symmetry-adapted pair $1s^2(^1S)$	$1s2s(^1S)$	$1s2s(^3S)$	$2s^2(^1S)$
ss	0.012 125	0.001 655	0.000 023	0.003 182
pp	0.022 490	0.001 684	0.000 415	0.001 843
dd	0.003 740	0.000 422	0.000 073	0.004 623
ff	0.001 042	0.000 116	0.000 012	0.001 303
gg	0.000 395	0.000 043	0.000 003	0.000 504
hh	0.000 179	0.000 020	0.000 001	0.000 233
ii	0.000 092	0.000 010	$<10^{-6}$	0.000 122
jj	0.000 052	0.000 006		0.000 069
kk	0.000 031	0.000 004		0.000 041
ll	0.000 020	0.000 002		0.000 027
Calculated pair energies	0.040 166	0.003 962	0.000 527	0.011 947
Extrapolated pair energies	0.040 22	0.003 97	0.000 53	0.012 02

[a] All energies in a.u. with signs reversed.

the $1s2s(^1S)$ pair this PW increment is still the largest, but the ss contribution is very close to it. The situation is quite different for the $2s^2(^1S)$ pair where dd contribution prevails and the role of the pp increment is very much reduced even with respect to ss. We tried to find the asymptotic rate of convergence of the energy increments with respect to l. It seems that for the singular pairs it is close to the l^{-4} law found by Schwartz,[34] although the convergence for the $2s^2$ pair is slightly slower than for the other pairs. In the case of the triplet $1s2s$ pair the convergence is like l^{-6}.

Sums of the PW increments representing the pair energies calculated according to Eq. (23) are also reported in Table II. It may be interesting to note that the second-order pair energy for the $2s^2$ pair is much smaller than for the $1s^2$ pair. In the last row extrapolated pair energies are displayed. The extrapolation procedure is of some importance only for the $1s^2$ and $2s^2$ pairs. For the latter pair the higher PW are relatively more important than for all other pairs, e.g., if one takes the sum of the three first PW increments one obtains for the $2s^2$ pair 80%, whereas for the other pairs, 95% of the total pair energy.

It seems interesting to compare the PW increments for the $(ns, n's)$ pairs in the case of a series of closed-shell atoms. Table III summarizes the results for He, Be, and Ne. In the case of the $1s^2(^1S)$ pair a striking regularity of the three expansions may be disclosed. First of all, the patterns of convergence of the PW expansions are in all three cases very much alike. There are very little changes of the magnitude of individual contributions. The ss contribution slightly decreases when proceeding from He to Ne, whereas the pp decrement discloses an opposed tendency. For higher PW one can observe a very slight increase of the second-order energy increments when proceeding to larger atoms. It seems, that to disclose all subtleties of the behavior of the PW expansions one should perform computations for all three atoms with the same accuracy. However, even now one can say that, in the case of dynamical pairs,[2,35] not only the total correlation energy but also the individual PW increments are approximately transferable. The latter fact is an additional argument in favor of a more extensive use of the PW language.

Comparison of the $1s2s(^1S)$ and $1s2s(^3S)$ expansion for Be and Ne also reveals a strong regularity. All PW increments are larger in the case of the Ne atom. The same is true for all but one contributions to the $2s^2$ pair energy. In the latter case the pp increment for Ne is much smaller than for Be. This sudden decrease is caused by the fact that in Ne there are no unoccupied $2p$ orbitals which are quasidegenerate like for Be with the $2s$ orbitals considered. Therefore, the $2s^2$ pair, which is nondynamical[35] in Be, becomes dynamical[35] for Ne.

In Table IV, PW contributions for the $(ns, 2p)$ pairs are reported. The main component for the $1s2p$ pairs is provided by the pd wave, whereas for the $1s2p$ pair the sp wave gives the dominant contribution. The convergence for the singlet pairs is rather slow. The higher terms behave approximately like $[\frac{1}{2}(l'+l'')]^{-4}$. The convergence in the case of the triplet pairs seems to be like $[\frac{1}{2}(l'+l'')]^{-6}$. In both cases the convergence is

TABLE III. Comparison of partial-wave increments to the second-order pair energy for He, Be, and Ne.[a]

l		$1s^2(^1S)$	
	He[b]	Be[c]	Ne[d]
0	0.013 47	0.012 47	0.012 13
1	0.018 94	0.022 48	0.022 49
2	0.003 17	0.003 55	0.003 74
3	0.000 92	0.001 01	0.001 04
4	0.000 35	0.000 39	0.000 40
5	0.000 16	0.000 18	0.000 18
6	0.000 08	0.000 09	0.000 09

	$1s2s(^3S)$		$1s2s(^1S)$		$2s^2(^1S)$	
	Be[c]	Ne[d]	Be[c]	Ne[d]	Be[c]	Ne[d]
0	0.000 014	0.000 023	0.001 030	0.001 655	0.002 26	0.003 18
1	0.000 663	0.000 415	0.001 819	0.001 684	0.022 14	0.001 84
2	0.000 050	0.000 073	0.000 246	0.000 422	0.003 82	0.004 62
3	0.000 008	0.000 012	0.000 074	0.000 116	0.001 19	0.001 30
4	0.000 002	0.000 003	0.000 028	0.000 043	0.000 48	0.000 50
5	0.000 001	0.000 001	0.000 013	0.000 020	0.000 23	0.000 23
6	$<10^{-6}$	$<10^{-6}$	0.000 006	0.000 010	0.000 12	0.000 12

[a] In atomic units with signs reversed.
[b] Byron and Joachain (Ref. 17).
[c] Webster and Steward (Ref. 19).
[d] This work.

slightly faster for the $1s2p$ pairs. The calculated pair energies for the pairs considered are also reported in Table IV. One can see that, according to the common intuitions, the correlation energies for individual singlet pairs are larger than for the corresponding triplets ones. This difference is especially pronounced for the $2s2p$ pairs. The pair energies for the $2s2p$ pairs are considerably larger than for the $1s2p$ pairs.

The PW contributions to the three $2p^2$ pairs are reported in Table V. For all pairs considered, the *pp* and *dd* waves provide the main contributions. The *ss* wave does not contribute to the ^3P and ^1D pairs, and is of little importance for the ^1S pair. The convergence characteristic is rather complicated. For the $2p^2(^1S)$ pair and the $l'l'$ part

TABLE IV. Partial-wave contributions $E^{(2)}(A)$ and pair energies for the $(ns, 2p)$ pairs.[a]

Partial-wave contributions	Symmetry-adapted pair $1s2p(^1P)$	$1s2p(^3P)$	$2s2p(^1P)$	$2s2p(^3P)$
sp	0.000 079	0.000 678	0.008 158	0.002 016
pd	0.002 005	0.000 783	0.004 198	0.000 509
df	0.000 405	0.000 067	0.004 834	0.000 349
fg	0.000 121	0.000 012	0.001 518	0.000 065
gh	0.000 048	0.000 003	0.000 626	0.000 018
hi	0.000 022	0.000 001	0.000 304	0.000 006
ij	0.000 010	$<10^{-6}$	0.000 164	0.000 002
jk	0.000 006		0.000 095	$<10^{-6}$
kl	0.000 003		0.000 059	
Calculated pair energies	0.002 690	0.001 544	0.019 956	0.002 965
Extrapolated pair energies	0.002 71	0.001 56	0.020 11	0.002 98

[a] All energies in a.u. with signs reversed.

TABLE V. Partial-wave contributions $E^{(2)}(A)$ and pair energies for the $2p^2$ pairs.[a]

Partial-wave contributions	$2p^2(^1D)$	$2p^2(^1S)$	$2p^2(^3P)$
ss	...	0.002 294	...
pp	0.008 011	0.015 207	0.004 582
dd	0.004 651	0.020 777	0.004 485
ff	0.000 664	0.004 300	0.000 486
gg	0.000 192	0.001 469	0.000 102
hh	0.000 076	0.000 637	0.000 030
ii	0.000 036	0.000 321	0.000 011
jj	0.000 020	0.000 178	0.000 006
kk	0.000 011	0.000 106	0.000 002
ll	0.000 007	0.000 067	0.000 001
sd	0.001 339		
pf	0.000 789		
dg	0.000 988		
fh	0.000 372		
gi	0.000 170		
hj	0.000 089		
ik	0.000 050		
jl	0.000 030		
Calculated pair energies	0.017 495	0.045 356	0.009 705
Extrapolated pair energies	0.017 57	0.045 56	0.009 71

[a] Energies are in a.u. with signs reversed.

of the $2p^2(^1D)$ pair the convergence rate is intermediate between the l^{-3} and l^{-4} laws. For the higher terms, convergence is a little bit slower than $[\frac{1}{2}(l'+l'')]^{-4}$. In the case of the triplet pair the convergence rate is slightly slower than given by the l^{-6} law.

For the intrashell $2p^2$ pair energies the most significant contribution is due to the ^1S pair. In turn, the ^3P pair energy is almost five times smaller. However, due to the high value of the pair weight $g(T)$ the triplet pair contributes more to E_2 than the ^1S pair.

Turning now to the whole set of pair energies for Ne, we compare in Table VI our results with those of some previous calculations. The results of Nesbet[33] were obtained within his Bethe-Goldstone approach, whereas the pair energies of Weiss[26] were calculated for each pair by CI calculations involving doubly excited configurations. However, these energies seem to be by several percents higher than their accurate counterparts. This is due both to the fact that the angular functions involve only *spdf* orbitals as well as to the incompleteness of the radial basis. As may be seen in Table VI the values of the pair energies of Nesbet and Weiss exhibit the same behavior as our results. However, the most interesting seems to be the comparison with the second-order pair energies of Pan and King[20] (PK) also obtained within the framework of the RS-HFPT within the VP approach. One can see that for the $(ns,n's)$ pairs their results are very close to ours. Yet, the energies for pairs involving p electrons differ considerably. The difference is especially pronounced for the $2p^2(^3P)$ pair where it amounts to 30% of the PK pair energy. For the $1s2p(^3P)$, $2s2p(^3P)$, and $2p^2(^1S)$ the results differ by 14%, 21%, and 14%, respectively. The best coincidence may be observed for the $2s2p(^1P)$ pair, in which

TABLE VI. Comparison of second-order pair energies $E_{ij}(T)$ with other works.[a]

Type of pair	Nesbet (Ref. 33)	Weiss (Ref. 26)	Pan and King (Ref. 20)	This work Calculated	This work Extrapolated
$1s^2(^1S)$	0.039 93	0.039 4	0.040 10	0.040 17	0.040 22
$1s2s(^3S)$	0.000 47	...	0.000 51	0.000 53	0.000 53
$1s2s(^1S)$	0.003 73	...	0.003 80	0.003 96	0.003 97
$2s^2(^1S)$	0.010 83	0.010 5	0.012 00	0.011 95	0.012 02
$1s2p(^3P)$	0.001 48	...	0.001 34	0.001 54	0.001 56
$1s2p(^1P)$	0.002 19	...	0.002 42	0.002 70	0.002 71
$2s2p(^3P)$	0.003 30	0.002 57	0.002 47	0.002 97	0.002 98
$2s2p(^1P)$	0.017 29	0.016 3	0.018 97	0.019 96	0.020 11
$2p^2(^3P)$	0.010 91	0.010 0	0.007 48	0.009 71	0.009 71
$2p^2(^1D)$	0.016 50	0.016 5	0.015 96	0.017 50	0.017 57
$2p^2(^1S)$	0.044 08	0.043 6	0.039 81	0.045 36	0.045 56

[a] In a.u. with all signs reversed.

case the pair energies differ by only (5–6)%. This comparison indicates that the pair energies of PK for the $1s2p$, $2s2p$, and $2p^2$ pairs are farther away from their exact counterparts than was anticipated by those authors, who expected to be in error by less than 5%. It seems that these large, in comparison with the situation for $(ns,n's)$ pairs, discrepancies of the results of PK is caused by the fact that the correlated trial functions, i.e., functions dependent explicitly on the interelectronic distances, may not be well suited for the descriptions of correlation effects for pairs involving p electrons. The reason of that fact may be understood basing on the present results. Let us note, that the basis functions of PK can be represented as CI-type functions involving s and p-type orbitals multiplied by certain scalar correlation factors. The latter are scalar products of two tensor operators. After recoupling, one may obtain functions in the PW form. However, for orbitals with $l>0$ the PW functions arise as linear combinations with fixed coefficients which may differ considerably from the variationally determined ones. Therefore, not all PW contributions may be obtained with sufficient accuracy.

The pair energies listed in Table VI are the only available in the literature. To get the possibility of a thorough comparison with previous works we present in Table VII shell-correlation energy contributions published by various authors. The first column shows the most accurate variational results reported so far. They were obtained by Sasaki and Yoshimine[36] by means of an exhaustive CI calculation using a basis set of 1571 configurations containing up to quadrupole excitations from a set of orbitals containing functions of s, p, d, f, g, h, and i symmetry ($l \leqslant 6$). The authors estimate their error to be of the order of (3–4)%. Results of various independent pair methods formulated within the framework of the variational approach are collected in the second column. The numbers represent the results of a summation over all pairs of the shells considered. The results for the K shell obtained by various authors do not differ much. Yet, for the KL- and L-shell contributions the discrepancies are significant. This situation is mainly caused by the fact that different basis sets have been used in various calculations. For example Bunge and Peixoto,[37] Weiss,[26] Viers, Harris, and Schaefer,[25] (VHS) and Moser and Nesbet[24] all use orbital basis sets limited to $1 \leqslant 3$ ($spdf$ limit). Barr and Davidson[7] applied their total-pair-excitation-block method using the orbital basis set restricted to functions with $l \leqslant 4$. Only Nesbet, Barr, and Davidson[7] calculated the Bethe-Goldstone pairs for the L shell with a nonoptimized basis set which included harmonics up to $l=6$. This is the reason why the total correlation energy obtained by those authors represents more than 105% of the "experimental" correlation energy. Although the saturation remainders due to the incompleteness of the basis sets have not been reported it seems that for complete basis sets the

TABLE VII. Comparison of K-, KL-, and L-shell correlation energy contributions for Ne. All energies are in a.u. with signs reversed.

Shell	Accurate CI (Ref. 36)	Various variational independent-pair approximations			CI-Hy (Ref. 23)	MBPT	Second-order perturbation method	
							Previous calculations	This work
K	0.0407	0.039 93 ^{a}	0.038 47 ^{b}	0.038 97 ^{c}	0.032 34	0.027 27 ^{d}	0.040 10 ^{e}	0.040 17 ^{f}
		0.039 93 ^{f}	0.039 4 ^{g}				0.037 64 ^{h}	0.040 22 ^{i}
KL	0.0266 ^{j}	0.025 03 ^{a}	0.023 26 ^{b}	0.024 37 ^{c}	0.015 21	0.027 58 ^{d}	0.024 65 ^{e}	0.027 54
	0.0276	0.024 02 ^{m}	0.026 55 ^{f}	0.023 1 ^{g}			0.024 11 ^{h}	0.027 73 ^{i}
		0.025 7 ^{o}						
L	0.2999 ^{j}	0.345 34 ^{k}	0.278 57 ^{b}	0.310 44 ^{c}	0.231 94	0.358 41 ^{d}	0.278 07 ^{e}	0.318 68
	0.3052 ^{l}	0.272 59 ^{m}	0.329 40 ^{f}	0.298 7 ^{g}		0.375 33 ^{n}	0.254 08 ^{h}	0.319 97 ^{i}
	0.322 ^{i}	0.331 5 ^{o}						

[a] Nesbet (Ref. 33).
[b] Bunge and Peixoto (Ref. 37).
[c] VHS- spinorbital pairs (Ref. 25).
[d] Lee, Dutta, and Das (Ref. 21).
[e] Pan and King (Ref. 20).
[f] Barr and Davidson (Ref. 7).
[g] Weiss (Ref. 26).
[h] Binkley and Pople (Ref. 38).
[i] Estimated results.
[j] Singly and doubly excited configurations.
[k] Nesbet, Barr, and Davidson (Ref. 39).
[l] Singly to quadruply excited configurations.
[m] VHS- irreducible pairs (Ref. 25).
[n] Prime and Robb (Ref. 40).
[o] Moser and Nesbet (Ref. 24).

sum of pair-correlation energies would overestimate the correlation energy by about 10%.

Table VII lists also the results of the combined configuration-interaction-Hylleraas (CI-Hy) calculations of Clary and Handy[23] which include explicitly correlated wave functions. One can see from Table VII that the KL- and L-shell subtotals of the correlation energy are smaller than the other results. This fact seems to confirm the statement made above, when discussing the pair energies of PK, that the correlation in p^2 and sp pairs is comparatively poorly represented by explicitly correlated wave functions. In closing the discussion of the variational-shell contributions, we would like to mention that our results are in good agreement with their most accurate counterparts obtained within the variational approach. The particularly close agreement of our L-shell result with the estimated value of Sasaki and Yoshimine seems to be encouraging. We would like to add that our energies are practically free from the radial basis saturation error.

Turning now to the results of the perturbation methods, we start with the comparison of the second-order shell contributions. One can see from Table VII that our shell subtotals are significantly lower than their counterparts obtained by Pan and King[20] and Binkley and Pople[38] within the RS-HFPT approach. We have already discussed the source of the difference with the results of the former authors. The difference with the latter authors is mainly due to the fact that they work within spd limit $(1 \leqslant 2)$.

It is of considerable interest to compare our results with the exhaustive calculations of Lee, Dutta, and Das[21] (LDD) within the framework of the linked-cluster many-body perturbation theory (LCMBPT). Results of the latter paper are considered by many authors as representative for the discussion of the relative importance of various many-body effects. One can see from Table VII that the results of LDD differ from other perturbational results. First, the K-shell ($1s^2$-pair) contribution differs by 30% from the average of all other results. It should be mentioned that by including contributions from various ladder diagrams this result is supposed to take into account the fact that due to the use of a V^{N-1} potential the $1s$ orbital differs from the exact RHF one. LDD suggest that the disparity is somehow distributed among other pair correlation energies. However, nothing like this was observed for the $1s^2$ pair in Be.[42] Second, the L-shell contribution of LDD is larger than obtained by other authors. This is especially true for the perturbation results. To get a better insight, one may compare the configuration pair energies, i.e., the sum of all pair energies determined by the same pair of orbitals

$$E_{ij}=\sum_{T} g(T)E_{ij}(T)\,, \tag{25}$$

where $E_{ij}(T)$ is defined by Eq. (23). Results for the L shell are listed in Table VIII. One can see that the difference between the LCMBPT results and the second-order values are the largest for the $2p^2$ pair. The results of LDD represent pair energies including contributions from hole-hole interactions, rearrangement corrections, hole-particle, and particle-particle diagrams summed up to all orders. If these corrections are neglected, the pair-energy contributions increase even

TABLE VIII. Comparison of configurational pair contributions for the L shell.[a]

		Second-order perturbation method		
ϵ_{ij}	MBPT	Previous calculations	This work	Variational pair energies (Ref. 7)
$2s^2$	0.012 68[b] 0.012 51[d]	0.012 00[c] 0.009 26[e]	0.011 95	0.011 17
$2s2p$	0.094 91[b] 0.081 52[d]	0.079 14[c] 0.058 24[e]	0.086 55	0.084 78
$2p^2$	0.250 82[b] 0.265 82[f] 0.281 28[c]	0.186 93[c] 0.186 58[e]	0.220 18	0.233 45

[a] All energies are in a.u. with signs reversed.

[b] LDD (Ref. 21).

[c] Pan and King (Ref. 20).

[d] Prime and Robb (Ref. 40).

[e] Binkley and Pople (Ref. 38).

[f] LDD contributions from second-order diagrams.

more as may be seen for the $2p^2$ pair, where to the pure second-order diagrams corresponds the energy of -0.26582. This value should be compared with the second-order energies listed in the third and fourth columns. The difference amounts to 21% of our result. To make a more-detailed comparison possible, we calculated the PW increments to the $2p^2$ orbital pair-correlation energy. These values are compared in Table IX with the results corresponding to the second-order diagrams reported by LDD.[21] One can see from Table IX that the largest differences arise for the *pp* and *dd* PW's. These discrepancies account for 97% of the difference between the two $2p^2$ orbital pair-correlation energies considered. Therefore, special attention has been paid to the problem of completeness of the radial basis set. As mentioned in Sec. III for these two PW's various basis sets specially chosen to minimize the energy decrements have been used. However, we were not able to reduce the difference further.

We realize that due to the fact that the LDD approach differs from ours in the choice of H_0, complete quantitative agreement of the second-order energy is not to be expected. However, the orbitals of the *L* shell are very close to ours (the 2*s* is exactly identical with ours) and one would expect that the pair-correlation energies are very much the same. This point of view has also been expressed by PK who first noted the discrepancies for the $2p^2$ orbital pairs. The difference of the $2p^2$ increments is for our results only 58% of that found by the latter authors. However, as has been indicated in Sec. III we have eliminated to a large extend the radial saturation error. Therefore, the difference is due either to the different choices of the potential in H_0 or to some numerical inaccuracies in the work of LDD. If the first possibility takes place, our results would be a strong argument for the advocates of the V^N potential. This is due to the fact, that the second-order pair energies yield almost 100% of the total correlation energy. To obtain comparable results within the LCMBPT using V^{N-1} one has to take into account a large number of complicated higher-order graphs. In Tables VII and VIII we also list the MBPT results of Prime and Robb[40] obtained in a discrete orbital basis set. The $2p^2$ pair contributions of those authors differ even more from our results than the LDD ones. However, this additional difference may be caused by the incompleteness of their Gaussian-type basis set. To obtain reasonable agreement with our results Prime and Robb had to take into account very complicated higher-order graphs.

Let us further consider the total second-order energy. We present in Table X a detailed breakdown of E_2 in terms of PW increments defined as

$$E^{(2)}(l'l'')=\sum_{ij}\sum_{T}{}'g(T)E^{(2)}(l',l'',i,j,T)\,. \tag{26}$$

These results allow us to grasp an idea about the character of the convergence of the PW expansion. Since the convergence patterns of the CI and perturbation expansion are very much alike, the increments given in Table X may be also useful for the analysis of accurate variational results. One can see from Table X that taking $l'l'' \leqslant 3$, 5, 7, and 9 one obtains 92.8%, 97.9%, 98.9%, and 99.3% of the "experimental" correlation energy (E^c_{expt}).

Closing this discussion of E_2 we compare in

TABLE IX. Contributions to the $2p^2$ pair-correlation energies from different partial waves.[a]

Partial wave	This work	Lee, Dutta, and Das[b]
ss	0.002 294	0.002 97
pp	0.096 500	0.124 14
dd	0.084 397	0.101 31
ff	0.011 994	0.014 53
gg	0.003 347	0.003 31
hh	0.001 287	0.001 16
ii	0.000 600	0.000 48
sd	0.006 695	0.007 62
pf	0.003 945	0.004 00
dg	0.004 940	0.004 35
fh	0.001 860	0.001 39
gi	0.000 850	0.000 56
Total $2p$–$2p$ correlation energy	0.220 19	0.265 28

[a] Energies is a.u. with signs reversed.

[b] Reference 21.

TABLE X. Breakdown of the total second-order correlation energy into partial-wave contributions. Energies are in units of 10^{-5} a.u. with all signs reversed.

$l'l''$	$\epsilon^{(2)}(l'l'')$	$l'l''$	$\epsilon^{(2)}(l'l'')$	$l'l''$	$\epsilon^{(2)}(l'l'')$
ss	19 325	*sp*	48 957	*sd*	6 695
pp	123 762	*pd*	30 237	*pf*	3 945
dd	93 401	*df*	19 461	*dg*	4 940
ff	14 491	*fg*	5 610	*fh*	1 860
gg	4 298	*gh*	2 211	*gi*	850
hh	1 722	*hi*	1 041	*hj*	445
ii	824	*ij*	540	*ik*	250
jj	459	*jk*	303	*jl*	150
kk	255	*kl*	186		
ll	160				
Subtotal	258 697	Subtotal	108 546	Subtotal	19 135
Total E_2		386 378			

Table XI the most important results for the correlation energy of Ne obtained by the above-mentioned authors. Essentially the results reflect the behavior already disclosed for the L shell. Most of the variational results are affected by some basis-saturation error. The best agreement with E^c_{expt} has been obtained by LDD. One can also see from Table XI that our second-order energy represents 99.3% of E^c_{expt}, whereas the estimated value amounts to 99.7% of the latter energy. Another result listed in Table X deserves some comment. This concerns the second-order energy obtained by Barr and Davidson[7] within the framework of a perturbation approach involving a partition of the Hamiltonian matrix for a basis containing ϕ_{HF}. Their result represent 121% of the correlation energy. This E_2 value has been extrapolated by Musher[3] to 132% of E^c_{expt}. The latter result certainly discourages from using second-order HF perturbation theory. We hope that the present work will lead to a revision of such pessimistic opinions. Barr and Davidson also used their E_2 to oppose conclusions reached by other authors concerning the relative importance of pair-pair interactions and ladder diagrams.[7] It seems, however, that their formulation provides the second-order energy so far from the accurate value, that the conclusions about the behavior of higher-order terms may not be transferable to the approaches used by other authors.

V. THIRD-ORDER ENERGY

To be sure that our second-order energy really represents a reliable result, one has to gain some insight into the structure of the perturbation series. First, one should inspect the magnitude of the higher-order terms to find out whether good agreement is due to fast convergence of the perturbation series or rather to a coincidence, and if the results will deteriorate if higher members of the series are taken into account. We concentrate our attention on the third-order term.

The third-order energy may be expressed in terms of the first-order function as[10]

$$E_3 = \langle \Psi_1 | H_1 - E_1 | \Psi_1 \rangle \,. \qquad (27)$$

In the variational-perturbation approach Ψ_1 is approximated by the function χ minimizing the Hylleraas functional Eq. (10). Hence, we approximate E_3 by

$$\begin{aligned} E_3 &\simeq \langle \chi | H_1 - E_1 | \chi \rangle \\ &= \langle \chi_{\text{TRA}} + \chi_{\text{TER}} | H_1 - E_1 | \chi_{\text{TRA}} + \chi_{\text{TER}} \rangle \,. \qquad (28) \end{aligned}$$

with the notation of Sec. II. Due to the two-electron character of H_1, the calculation of E_3 is

TABLE XI. Comparison of the total correlation energy for Ne. All energies in a.u. with signs reversed.

Method	Authors	Total correlation energy		
CI	Sasaki and Yoshimine (Ref. 36)	0.3627 [a]	0.3697 [b]	0.3896 [c]
	Bunge and Peixoto (Ref. 37)	0.3403		
	Barr and Davidson (Ref. 7)	0.3333		
	Ahlrichs *et al.* (Ref. 41)	0.3236		
Variational-pair approximations	Nesbet (Ref. 33)	0.4103		
	VHS (Ref. 25)	0.3356 [d]	0.3738 [e]	
	Weiss (Ref. 26)	0.3612		
	Ahlrichs *et al.* (Ref. 41)	0.3726		
CEPA	Ahlrichs *et al.* (Ref. 41)	0.3338		
CI-Hy	Clary and Handy (Ref. 23)	0.2795		
MBPT	LDD (Ref. 21)	0.3891	0.4134 [f]	
Second-order perturbation theory	Pan and King (Ref. 20)	0.3428		
	Binkley and Pople (Ref. 38)	0.3158		
	Barr and Davidson (Ref. 7)	0.4709		
	This work	0.38638	0.3879 [c]	
"Experimental" correlation energy (Ref. 21)		0.3890 ± 0.001		

[a] Singly and doubly excited configurations.
[b] Singly to quadruply excited configurations.
[c] Extrapolated result.
[d] Spin-orbital pairs.
[e] Irreducible pairs.
[f] Sum-of-pair energies.

rather complicated and requires the same types of integrals as the purely variational method.

We have discussed in Sec. II A the main idea of computing matrix elements for functions containing SAPFs.

Since the computer time needed for the calculation of E_3 is close to that required by a variational calculation with the same basis set, we could not effort to accomplish the computations with the same accuracy as indicated in Sec. III, i.e., using the full set of 13 880 configurations. Therefore, we performed another second-order calculation using smaller sets of radial basis functions, and limited ourselves to the most significant PW, e.g., for the $2p^2(^3P)$ pair we used radial bases of dimensions containing 36, 15, 6, and 3 functions for the *pp*, *dd*, *ff*, and *gg* PW's, respectively. Some energy increments obtained in this calculation are listed in the last column of Table XII.

The E_2 value obtained is − 0.34203 a.u. compared with our most-accurate value of − 0.38638. Although the former result is affected by an error of about 11% it is still very close to the best E_2 obtained so far (Pan and King— − 0.3428 a.u.).

The third-order energy evaluated with the simpler first-order wave function is + 0.002446 a.u. We know of two attempts of evaluating E_3 for Ne within the framework of RS-HFPT. The first result of − 0.00048 a.u. has been reported by Pople, Binkley, and Seeger.[5] The second value of + 0.00012 a.u. has been published very recently by Urban, Kollö, and Hubač.[8] The second-order energies obtained by these two groups have been of − 0.25452 and − 0.2149 a.u., respectively. Both results have been obtained within an approach which involves direct summation of the perturbation series. Therefore, the accuracies of their second-order energies are not so directly, as in our case, connected with the accuracy of E_3. However, their E_2 values provide some information about the completeness of the set of one-electron functions employed. It seems that both numbers are quite far from the exact third-order result. Our E_3 value, although computed with a first-order function, leading to more accurate E_2 is also expected to be affected by a significant error, which may be even as large as 20%. Our experience gained for Be indicates that when improv-

TABLE XII. Diagonal and some off-diagonal contributions to the third-order energy of Ne. Orbital pair increments to the second-order energy[a] (in a.u.).

Pairs	Diagonal contributions	Off-diagonal contributions involving specified types of pairs only.	Second-order energy increments[a]
$1s^2(^1S)$	−0.000 98		−0.038 99
$2s^2(^1S)$	−0.000 71		−0.010 23
$1s2s(^1S)$	−0.000 12		−0.003 63
$1s2s(^3S)$	−0.000 02		−0.000 46
$1s2s$	−0.000 18	0.000 01	−0.005 01
$1s2p(^1P)$	−0.000 24		−0.002 02
$1s2p(^3P)$	−0.000 06		−0.001 40
$1s2p$	−0.001 28	0.000 11	−0.018 66
$2s2p(^1P)$	−0.008 52		−0.015 33
$2s2p(^3P)$	−0.000 31		−0.002 81
$2s2p$	−0.028 35	0.003 23	−0.071 28
$2p^2(^1S)$	−0.003 13		−0.040 35
$2p^2(^3P)$	−0.000 69		−0.009 33
$2p^2(^1D)$	−0.001 81		−0.014 71
$2p^2$	−0.018 39	0.018 92	−0.197 87
	Sum of diagonal contributions	Total off-diagonal contributions	Total second-order energy[a]
	−0.049 89	0.052 38	−0.342 09[a]

Third-order energy
0.002 446

[a] Obtained for the first-order function used in the third-order calculation.

ing the accuracy of the first-order result the absolute value of E_3 decreases. In summary, we see that the third-order energy for Ne is very small, and the high accuracy of our second-order result is due to the fast convergence of the perturbation expansion.

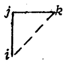
Although the estimation of E_3 has been the main motivation of our calculations, there has been another problem that attracted our attention. This was the problem of relative importance of diagonal and off-diagonal terms[18] in the expression for E_3. We use the terminology of Byron and Joachain who understood by diagonal terms the diagonal matrix elements in the basis of the $\chi_{\mathrm{TRA}}^{i,T_p}$, and $\chi_{\mathrm{TER}}^{ij,T_{ij}}$ function, i.e.,

$$\langle\chi_{\mathrm{TRA}}^{i,T_p}|H_1-E_1|\chi_{\mathrm{TRA}}^{i,T_p}\rangle \quad \text{or} \quad \langle\chi_{\mathrm{TER}}^{ij,T_{ij}}|H_1-E_1|\chi_{\mathrm{TER}}^{ij,T_{ij}}\rangle \tag{29}$$

All other terms are called off-diagonal. Basing on their estimates of typical terms of the off-diagonal type, Byron and Joachain[18] claimed that for the Be atom these terms contribute little to the third-order energy, and thus neglected them in their calculations. This is equivalent to a reduction of the problem of calculating E_3 for the N-electron system to the computation of the third-order energies for a set of two-electron problems defined by all possible electron pairs.

We report in Table XII all diagonal contributions to the third-order energy together with off-diagonal contributions involving pairs differing only in the symmetry designation. One can see from Table XII that all off-diagonal contributions are positive. They are in fact small for the $1s2s$, $1s2p$, and $2s2p$ pairs. However, for the $2p^2$ pairs the sum of all off-diagonal contributions is even slightly greater than the absolute value of the sum of all diagonal contributions. We see that for the $2p$ shell of Ne one cannot omit the off-diagonal terms, and therefore a reduction of the N-electron problem to a set of two-electron problems is not possible if accuracy up to third-order is considered. If one uses the nomenclature of Pople *et al.*[5] the sum of diagonal contributions can be considered as a counterpart of their $E_{\mathrm{IEPA}}^{(3)}$. In turn, the off-diagonal terms represent pair-pair interactions. Our results indicate that for the Ne atom the $E_{\mathrm{IEPA}}^{(3)}$ and pair-pair interaction contributions almost cancel, which is in agreement with the conclusion of Pople *et al.*[5] It may be interesting to compare our value of the diagonal contributions with the result for $E_{\mathrm{IEPA}}^{(3)}$ reported by Pople *et al.*[5] The values are -0.04994 and -0.03511 a.u., respectively. The ratio of these two contributions is almost equal to the ratio of ours and Pople's *et al.*[5] second-order energies. Our off-diagonal contributions for the $2p^2$ pairs, 0.01892, and for the $2s2p$ pairs 0.00324, may be compared with the results of Prime and Robb[38] for the pair-pair repulsion corrections which are 0.02382 and 0.00509, respectively. The ratio of the off-diagonal contribution for the $2p^2$ pair to the sum of the second-order energy and the diagonal third-order terms is 0.052 compared with the estimate value of 0.1 reported by Micha[43] for the ratio of many-body to two-body correlation energies for the $2p$ shell of Ne. Finally, one may from the entries of Table XII estimate the "two-body" terms of Sinanoğlu's theory,[44] $\sum_{i<j}(E_{ij}^{(2)}+E_{ij}^{(3)})$, and compare it with the "three- and more-electron" effects represented by the term

$$\sum_{i,j,k}$$



of that theory.[44] The results are -0.39198 and 0.05238 a.u. for the short expansion of the first-order wave function. If the accurate second-order energy is used, we obtain -0.4407 a.u. One can see that the two-body term overestimates the correlation energy by more than 10%.

VI. SUMMARY

We defined the atomic N-electron wave function of the independent-pair approximation in terms of orbital configurations and SAPF. This form has been chosen to fit the Condon-Shortley-Racah formulation of the theory of complex atomic configurations. Our formulation was used to set up a general variational-perturbation algorithm within the framework of the RS-HFPT. A general program for the computation of very accurate E_2 and E_3 energies has been developed and applied to the ground state of Ne.

Our formulation is equivalent to other variational-perturbation approaches. It offers, however, the possibility of performing computations for large atoms containing several closed shells of p, d, and f electrons.

It turned out that the perturbation expansion for the RS-HFPT is very fastly convergent for the system considered. Our E_2 result represents 99.3% of E_{exp}^{c} (the extrapolated value reproduces 99.7%). The E_3 value is about 0.5% of the second-order result. The sum E_2+E_3 indicates that the exact correlation energy is 0.3879 ± 0.002 a.u.

The pair functions are represented in a PW form, and the PW energy increments are obtained for all pairs. The comparison of the PW increments for the *ns*,*ns* pairs along the series He, Be, and Ne allows us to disclose very interesting regularities in the behavior of individual energy increments. This seems to confirm our opinion that the PW formulation represents a convenient tool for the investigation of correlation effects.

We have performed a detailed analysis of the relative importance of various PW contributions both for pair energies as well as second-order energy. It turned out that restricting the expansions to $l'l'' < 3$ one may get 92.8% of E^c_{expt}, whereas for $l'l'' \leq 9$ one obtains 99.3%. The PW analysis also sheds some light on the problem of the ineffectiveness of explicity correlated wave functions in describing correlation effects within the L shell.

The high accuracy of the present results make it possible to use them as reference points in discussions of other perturbation approaches. Therefore special attention is paid to the comparison with other work. We found, e.g., that the VP results of PK[28] may be considerably improved. On the other hand, the second-order energy obtained by LDD[21] within the framework of the LCMBPT based on the V^{N-1} potential significantly overestimate the correlation energy. The same is true for the individual orbital pair energies. The values of the latter are only slightly improved by taking into account the contributions due to hole-hole, rearrangement, hole-particle, and particle-particle higher-order diagrams. We also indicate that a perturbative method based on the partitioning of the Hamiltonian matrix in a way suggested by Barr and Davidson yields second-order energies which are very different from the standard RS-HFPT results and therefore may lead to inaccurate assessments of various correlation effects.

The results of the present work confirm the observation of Pople *et al.*[5] that the independent-pair contributions to the third-order energy almost cancel with the pair-pair increments, leading to an enormous reduction of E_3. This cancellation is especially effective for $2p^2$ pairs. Thus the procedure of Byron and Joachain[18] based on the neglect of off-diagonal terms is not applicable for larger atoms.

The very good agreement with E^c_{expt} obtained within a RS-HFPT formulation indicates that this conceptually simple method may be especially effective in dealing with correlation effects in larger atomic systems. Our general computer program allows to handle every closed-shell atom. Results for a system containing the $3d^{10}$ shell have already been obtained.[15] The main problem now is to investigate to what extent the success for Ne depends on the specific system chosen. Work along this line is in progress.

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APPENDIX: MATRIX ELEMENTS OF ONE- AND TWO-PARTICLE OPERATORS

Let us discuss the matrix elements of the operator U (a one- or two-particle operator) which arise from the expression

$$\Big(\phi_0(\bar{0}) + \sum_{i<j} \chi^{ij}_{\text{TER}}(\bar{0}) + \sum_i \chi^i_{\text{TRA}}(\bar{0}) \,|\, \hat{U} \,|\, \phi_0(\bar{0}) + \sum_{i<j} \chi^{ij}_{\text{TER}}(\bar{0}) + \sum_i \chi^i_{\text{TRA}}(\bar{0})\Big)\,, \tag{A1}$$

in the case when all pair functions involved are strongly orthogonal. It can be shown[31] that nonvanishing contributions are due to the following matrix elements:

(i) for any one-electron scalar operator, $\hat{F}$:

$$\text{(a) } [\phi_0(\bar{0})|\hat{F}|\phi_0(\bar{0})],\quad \text{(b) } [\chi^i_{\text{TRA}}(\bar{0})|\hat{F}|\chi^i_{\text{TRA}}(\bar{0})],$$
$$\text{(c) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{F}|\chi^{ij}_{\text{TER}}(\bar{0})],\quad \text{(d) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{F}|\chi^{jk}_{\text{TER}}(\bar{0})]$$
$$\text{(e) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{F}|\chi^i_{\text{TRA}}(\bar{0})]\,. \tag{A2}$$

(ii) for any two-electron scalar operator, $\hat{G}$:

$$\text{(a) } [\phi_0(\bar{0})|\hat{G}|\phi_0(\bar{0})],\quad \text{(b) } [\phi_0(\bar{0})|\hat{G}|\chi^{ij}_{\text{TER}}(\bar{0})],$$
$$\text{(c) } [\phi_0(\bar{0})|\hat{G}|\chi^i_{\text{TRA}}(\bar{0})],\quad \text{(d) } [\chi^i_{\text{TRA}}(\bar{0})|\hat{G}|\chi^i_{\text{TRA}}(\bar{0})],$$
$$\text{(e) } [\chi^i_{\text{TRA}}(\bar{0})|\hat{G}|\chi^j_{\text{TRA}}(\bar{0})],\quad \text{(f) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{G}|\chi^{ij}_{\text{TER}}(\bar{0})],$$
$$\text{(g) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{G}|\chi^{jk}_{\text{TER}}(\bar{0})],\quad \text{(h) } [\chi^{ij}_{\text{TER}}(\bar{0})|\hat{G}|\chi^{kl}_{\text{TER}}(\bar{0})],$$
$$\text{(i) } [\chi^i_{\text{TRA}}(\bar{0})|\hat{G}|\chi^{ij}_{\text{TER}}(\bar{0})],\quad \text{(j) } [\chi^i_{\text{TRA}}(\bar{0})|\hat{G}|\chi^{jk}_{\text{TER}}(\bar{0})]. \tag{A3}$$

In order to evaluate all such matrix elements one needs to carry out the following steps: (a) to apply the Wigner-Eckart theorem to the initial form of the matrix element and (b) to execute such successive changes of coupling schemes in the functions which separate out only these parts on which act the operators $\hat{f}_i$ or $\hat{g}_{ij}$.

Let us, for example, present the explicit expression for the matrix element between two intrashell contributions

$$\begin{aligned}
[\chi^{i}_{\mathrm{TRA}}(\bar{0})\,|\hat{G}|\,\chi^{i}_{\mathrm{TRA}}(\bar{0})] = {} & \frac{N_i(N_i-2)}{2}\sum_{T_p,T_p}(l_i^{N_i-2}(T_p),l_i^2(T_p)|\}l_i^{N_i}(0))(l_i^{N_i-2}(T_p')l_i^2(T_p')|\}l_i^{N_i}(0)) \\
& \times\Bigg(\delta(T_p,T_p')\Bigg\{\Bigg[\sum_{m\neq i}\frac{N_m(N_m-1)}{2}\sum_{T_m}(l_m^{N_m-2}(T_m),l_m^2(T_m)|\}l_m^{N_m}(0))^2\Gamma_{m,n}(T_m) \\
& \qquad +N_m(N_i-2)\sum_{T_{im}}(l_i^{N_i-3}(T_{im}),l_i|\}l_i^{N_i-2}(T_p))^2\Gamma_{i,m}(T_{im})+\frac{(N_i-2)(N_i-3)}{2} \\
& \qquad \times\sum_{T_1,T_1'}(l_i^{N_i-4}(T_1),l_i^2(T_1')|\}l_i^{N_i-2}(T_p))^2\Gamma_{i,i}(T_i') \\
& \qquad +\sum_{q<p}N_qN_p\sum_{T_{qp}}\left(\frac{T_{qp}}{t_q,t_p}\right)\Gamma_{q,p}(T_{qp})\Bigg]S^{i,i}(T_p) \\
& +\sum_{m\neq i}N_m\sum_{T_2}\left(\frac{T_2}{T_p,t_m}\right)\Delta^{i,i}_{m,m}(T_p,T_p;T_2)+\Theta^{i,i}(T_p)\Bigg\} \\
& +(N_i-2)\sum_{T_3}(l_i^{N_i-3}(T_3),l_i|\}l_i^{N_i-2}(T_p))(l_i^{N_i-3}(T_3),l_i|\}l_i^{N_i-2}(T_p'))\Delta^{i,i}_{i,i}(T_p,T_p';T_3)\Bigg)\,,
\end{aligned}$$

where

$$\Gamma_{m,n}(T)=[l_m(t_m|1),l_n(t_n|2);T\,\|\,g_{12}\,\|\,l_m(t_m|1),l_n(t_n|2);T]\,,$$

$$\Delta^{i,j}_{k,l}(T_1,T_2;T_3)=[l_k(t_k|1),u_i(T_1|2,3);T_3\,\|\,g_{12}\,\|\,l_1(t_1|1),u_j(T_2|2,3);T_3]\,,$$

$$S^{i,j}(T)=[u_i(T|1,2)|u_j(T|1.2)]\,,$$

$$\theta^{i,j}(T)=[u_i(T|1,2)\,\|\,g_{12}\,\|\,u_j(T|1,2)]\,.$$

The double vertical lines in these elements denote irreducible matrix elements. These elements can be readily expressed in terms of pure radial integrals and $3n$-j symbols.[31]

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