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Application of symmetry-adapted pair functions in atomic structure calculations. II. Third-order correlation energy of the neon atom

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The accurate third-order correlation energy (E_3) for Ne is evaluated within the framework of the Rayleigh-Schrödinger Hartree-Fock perturbation theory. The variational-perturbation method is applied. The N-electron first-order wave function is defined in terms of orbital configurations, of one-electron functions, and of symmetry-adapted pair functions in the form of partial-wave (PW) expansions. It is demonstrated that the value of E_3 critically depends on the accuracy of the approximate first-order wave function. In order to obtain accurate values of E_3, the pair functions have to be approximated in terms of extensive basis sets both in the radial and angular sense. A calculation based on all PW's up to $1',1'' \leq 9$ yields the value $E_3=0.003\,49$ hartree. Careful radial and angular extrapolations result in $E_3=0.0044$ hartree. The third-order energy is analyzed in terms of third-order pair energies and third-order PW increments to the pair energies. It is found that the third-order values modify the individual second-order PW increments and second-order pair energies by about 10%, whereas the modification caused by E_3 on the values given by E_2 is of the order of 1%. The stability of the third-order results with respect to the accuracies of the solution of the Hartree-Fock equations is also discussed.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as I, a variational-perturbation scheme for closed-shell systems was presented. It is based on the assumption $H_0=H_{\mathrm{HF}}$ and on the application of the N-electron first-order wave function expressed in terms of orbital configurations of one-electron functions and symmetry-adapted pair functions (see the fundamental papers of Sinanoglu, Ref. 2) in the form of partial-wave (PW) expansions. Owing to the structure of the approximate first-order wave function one can make extensive use of the simplifications provided by the application of the irreducible tensor-operator algebra. As a result, our method furnished the possibility of performing accurate second- and third-order calculations for larger atoms containing many closed shells of equivalent electrons. Thus far the main computational effort has been concentrated on the calculation of accurate second-order pair energies and PW increments for many closed-shell atoms up to the Zn-isoelectronic sequence.[1,3] There are many motivations for undertaking such large scale calculations of accurate second-order correlation energies.[4,5] Let us just mention two of the arguments: (a) There is much numerical evidence that the second-order energy E_2 represents for all but the smallest systems the bulk (more than 90%) of the total correlation energy,[2] e.g., we have found in I that for Ne E_2 represents 99.7% of the total "experimental" correlation energy. (b) The second-order calculations for complex closed-shell systems provide the only source of information about many details of the all-external (dynamical) correlation effects,[6] which can be used in setting up semiempirical methods for the study of correlation effects in arbitrary atomic systems.

A question immediately arises: How will the "second-order picture" of electron correlation in complex atoms change if higher-order terms of the perturbation expansion are taken into account? The next perturbative term to be considered is the third-order energy E_3. Since the structure of this quantity is much more complicated than of E_2, its accurate evaluation is a very difficult task, needing computer times close to those required by a variational calculation based on doubly excited configurations involving the same orbital basis set. In I we have presented the results of our preliminary attempt to the evaluation of E_3 for Ne using an approximate first-order wave function expressed in terms of a limited basis set (corresponding to $E_2 = 0.3421$ hartree, i.e., 89% of the extrapolated value). Recently, when performing very accurate coupled-cluster calculations by a method based on numerical solutions of the radial two-electron equations,[7] Lindgren and Salomonson[8] obtained also accurate E_2 and E_3 values for Ne. Their $E_3 = 0.0035$ hartree result differs significantly from our value of 0.002 45 hartree indicating that E_3 may be much more sensitive to the accuracy of the first-order wave function than E_2.

The object of the present paper is an attempt of accurate evaluation of the third-order energy and third-order pair energies for Ne within the framework of our approach. To secure this aim we approximate the pair functions in terms of many sets extensive both in the radial and angular sense. The numerical calculations are followed by careful extrapolations, aiming to remove the errors due to the limited character of our basis sets. We have developed an efficient computer program for the evaluation of E_3 for arbitrary closed-shell atoms. Our motivation for performing these extensive calculations of E_3 stems from the fact that the knowledge of the accurate values of the leading terms of the perturbational expansion of the correlation energy for some complex atomic systems is of importance from the methodological point of view. In the absence of any information about the exact value of the correlation energy for such systems these terms may play the role of a benchmark for the estimation of the reliability of various realizations of the perturbational approach, e.g., of the many-body perturbation theory (MBPT). The choice of Ne for the present calculations is caused by the fact that at present this atom posesses the status of the standard test system for all advanced methods of dealing with the electron-correlation problem. Another goal of this research is the analysis of the detailed structure of E_3. For this aim we analyze this quantity in terms of third-order pair energies and third-order PW increments which we shall define below. We have shown how these quantities are related to the accurate pair energies and PW increments obtained from the analysis of the accurate correlation energies. Therefore, our results provide some information on the direction of changes of the pair energies and PW increments when proceeding from the second-order level of accuracy to accurate, e.g., variational, results. This information may be useful for setting up semiempirical procedures of evaluating dynamical correlation effects in complex systems.[5]

Finally, it seems to us that our work may be interesting from the following point of view. A comparison of the present results with their counterparts obtained by Lindgren and Salomonson by a completely different method may shed some light on the magnitude of the uncertainties of the third-order results and stimulate further work to increase the accuracy of evaluation of the sensitive E_3 (and perhaps E_4) values.

Since the method employed here has been described in detail in I we present in Sec. II only new definitions concerning the analysis of the correlation energy in terms of symmetry-adapted pair energies and PW increments and some detailed formulas for the third-order values. In Sec. III we report some computational details relevant to the present work. The calculated and extrapolated third-order values of the PW increments, the pair energies, and the total energy are presented and discussed in Sec. IV. In this section we also discuss the impact of the approximate character of the HF orbitals on the results obtained and review shortly the third-order energies reported by various authors.

II. METHODOLOGY

The method has been presented in detail in I, where also all definitions pertinent to the second-order energy and first-order wave function have been given. Here we shall discuss in detail the third-order energy E_3 of closed-shell atoms. To this end we shall introduce some new definitions and simplify the notation both for the exact and perturbational solutions of the Schrödinger equation.

A. Symmetry-adapted formulation of the exact and perturbational problems

Let us consider the solution of the Schrödinger equation

$$H\Psi = E\Psi \tag{1}$$

for the closed-shell ground state of an N-electron atom. We write the Hamiltonian as

$$H = H_0 + H_1 , \tag{2}$$

where we assume H_0 in the HF form, i.e.,

$$H_0 = H_{\mathrm{HF}} = \sum_{i=1}^{N} h(i) \tag{3}$$

and $h(1)$ denotes the one-electron Fock operator.[9] We have

$$H_1 = H - H_0 = \sum_{i<j}^{N} r_{ij}^{-1} - \sum_{i=1}^{N} V(i) \qquad (4)$$

with $V(i)$ denoting the sum of the Coulomb and exchange operators.

Let us write Ψ as

$$\Psi = \Psi_0 + \chi , \qquad (5)$$

where $\Psi_0 = \Psi_{\rm HF}$ is an eigenfunction of H_0 belonging to the eigenvalue $E_{\rm HF}$. We assume that Ψ is given in the intermediate normalization,

$$\langle \Psi_0 | \Psi \rangle = \langle \Psi_0 | \Psi_0 \rangle = 1, \quad \langle \Psi_0 | \chi \rangle = 0 . \qquad (6)$$

Now the exact energy E can be written as

$$E = \langle \Psi_0 | H | \Psi \rangle = E_{\rm HF} + \langle \Psi_0 | H | \chi \rangle . \qquad (7)$$

The last matrix element represents the correlation energy

$$E_{\rm corr} = E - E_{\rm HF} = \langle \Psi_0 | H | \chi \rangle \qquad (8)$$

and the function χ is often referred to[9] as the exact correlation function. By making use of the Brillouin theorem and of the fact that H_1 contains at most two-particle interactions, one can write

$$E_{\rm corr} = \langle \Psi_0 | H_1 | P^{(2)} \chi \rangle , \qquad (9)$$

where $P^{(2)}$ denotes the projection operator into the subspace spanned by all configurations, doubly excited with respect to the HF state Ψ_0. Owing to the fact that $E_{\rm corr}$ is determined only by the $P^{(2)}\chi$ function, $E_{\rm corr}$ can be analyzed in terms of pair contributions defined in various ways. We shall use symmetry-adapted pairs (see I) and write $P^{(2)}\chi$ for closed-shell systems (we omit the symmetry designation $L = S = M_L = M_S = 0$) in the general form introduced in Appendix A:

$$P^{(2)}\chi = \sum_K \mathscr{A}^K \sum_T a_T^K \{ \Phi_0^K(T \mid N-2) u^K(T \mid 2) \} , \qquad (10)$$

where T is shorthand for the pair of L,S quantum numbers,

$$T \leftrightarrow (L,S) . \qquad (10')$$

We shall use this notation throughout the paper in all cases whenever misunderstanding is excluded. Since χ represents the exact correlation part of the N-electron wave function, $u^K(T \mid 2)$ may be termed an "exact" symmetry-adapted pair function (SAPF) describing the Kth configurational pair characterized by the eigenvalues $T \equiv (L,S)$ of the angular momenta operators. Of course, $u^K(T \mid 2)$ is strongly orthogonal to $\Phi_0^K(T \mid N-2)$ and to the symmetry-adapted pair function $u_0^K(T \mid 2)$ defined in Appendix A. As we have shown in Appendix B, inserting (10) into (9) one obtains

$$E_{\rm corr} = \sum_K \sum_T g(T) E^K(T) , \qquad (11)$$

where

$$g(T) = g(L,S) \equiv (2L+1)(2S+1) \qquad (12)$$

and

$$E^K(T) = \langle u_0^K(T) | g | u^K(T) \rangle \qquad (13)$$

represents the exact correlation energy of the Kth pair with the T-symmetry designation. It is often useful to represent the exact SAPF's in terms of the PW expansion (Appendix B)

$$u^K(T \mid 2) = \sum_{l,l'} u(l,l',K,T \mid x_1, x_2) , \qquad (14)$$

and express the pair energy as a sum of the exact PW increments

$$E^K(T) = \sum_{l,l'} E(l,l',K,T) , \qquad (15)$$

with

$$E(l,l',K,T) = \langle u_0^K(T \mid 2) | g | u(l,l',K,T) \rangle . \qquad (16)$$

Let us now turn to the Rayleigh-Schrödinger HF perturbation theory taking $H_0 = H_{\rm HF}$. Denoting by Ψ_i the ith-order wave function, and remembering that $\Psi_0 = \Psi_{\rm HF}$ we obtain

$$\chi = \sum_{i=1}^{\infty} \Psi_i \qquad (17)$$

and

$$E_{\rm corr} = \sum_{i=2}^{\infty} E_i \qquad (18)$$

with

$$E_{i+1} = \langle \Psi_0 | H | P^{(2)} \Psi_i \rangle . \qquad (19)$$

We know from I that Ψ_1 is exactly expressible in terms of doubly-excited configurations, i.e., $P^{(2)}\Psi_1 = \Psi_1$.

Now, one can represent easy $P^{(2)}\chi_i$ in the symmetry-adapted form (A5) using the ith-order SAPF's. Taking the sum of those expressions and comparing with Eq. (10) for $P^{(2)}\chi$ we obtain an expansion of the exact SAPF in terms of the ith-order SAPF's

$$u^K(T\,|\,2)=\sum_{i=1} u_i^K(T\,|\,2)\ . \tag{20}$$

Inserting (20) into (13) leads to

$$E^K(T)=\sum_{i=1}^{\infty} E_i^K(T)\ , \tag{21}$$

where the ith-order correction to the energy of the Kth pair is given by

$$E_{i+1}^K(T)=\langle u_0^K(T)\,|\,g\,|\,u_i^K(T)\rangle\ . \tag{22}$$

From (19) we have, of course,

$$E_i=\sum_K\sum_T g(T)E_i^K(T)\ . \tag{23}$$

Similarly, the exact PW increments to the pair energies (16) may be formally decomposed into contributions from consecutive orders of the perturbation expansion

$$E(l,l',K,T)=\sum_{i=1}^{\infty} E_i(l,l',K,T)\ . \tag{24}$$

B. Third-order energy corrections

Equations (19), (22), and (24) expressing the ith-order contribution to the pertinent energy value in terms of the ith-order functions are very inconvenient from the practical point of view. It is well known[10] that one can obtain the perturbation energy to the $(2i+1)$th order from the knowledge of the wave function perturbed to the ith order, e.g., the third-order energy may be expressed in two different ways,[10]

$$E_3=\langle \Psi_0\,|\,H_1\,|\,\Psi_2\rangle\ , \tag{25a}$$

$$E_3=\langle \Psi_1\,|\,H_1-E_1\,|\,\Psi_1\rangle\ , \tag{25b}$$

where the first form corresponds to Eq. (19). Hence, knowing the first-order wave function we are in a position to evaluate the total third-order energy. According to (23) E_3 can be analyzed in terms of the third-order pair energies

$$E_3^K(T)=\langle u_0^K(T)\,|\,g\,|\,u_2^K(T)\rangle\ . \tag{26}$$

This equation is inconvenient for our goal because it involves the second-order SAPF. However, it is possible to reexpress E_3^K only in terms of the first-order SAPF's $u_1^K(T\,|\,2)$. To this aim let us write Ψ_1 as

$$\Psi_1=\sum_K\sum_T \Psi_1(K,T) \tag{27}$$

with

$$\Psi_1(K,T)=a_T^K\mathscr{A}^K\{\,\Phi_0^K(T\,|\,N-2)u_1(T\,|\,2)\,\}\ . \tag{28}$$

As we show in Appendix C, E_3^K can be written as

$$E_3^K(T)=g(T)^{-1}\langle \Psi_1(K,T)\,|\,H_1-E_1\,|\,\Psi_1\rangle\ . \tag{29}$$

Let us note that the third-order correction to the energy of the Kth pair depends on the first-order SAPF's of all pairs.

For our purpose it is also convenient to cast the expression for the third-order PW increments to the pair energies, defined according to Eqs. (24), (16), and (B9) as

$$E_3(l,l',K,T)=\langle u_0^K(T\,|\,2)\,|\,g\,|\,u_2(l,l',K,T)\rangle\ , \tag{30}$$

into a form dependent on the first-order PW increments. To achieve this we introduce the function

$$\Psi_1(l,l',K,T)=a_T^K\mathscr{A}^K\{\Phi_0^K(T\,|\,N-2)u_1(l,l',K,T)\}\ . \tag{31}$$

It is easily seen that

$$\Psi_1(K,T)=\sum_{l,l'}\Psi_1(l,l',K,T) \tag{32}$$

and

$$\Psi_1=\sum_K\sum_T\sum_{l,l'}\Psi_1(l,l',K,T)\ . \tag{33}$$

TABLE I. Parameters of the radial basis functions $R(n,\eta\,|\,r)$.

No.	n	η	No.	n	η
1	1	25.395	11	5	9.249
2	3	44.776	12	3	5.577
3	2	25.395	13	6	8.284
4	3	25.395	14	4	5.577
5	4	25.395	15	5	5.577
6	5	25.395	16	2	2.675
7	2	11.608	17	6	5.577
8	3	11.608	18	3	2.675
9	4	11.608	19	4	2.675
10	2	5.577	20	5	2.675

Now, using the first-order-type function $\Psi_1(l,l',K,T)$ one can show, in a similar manner as for $E_3^K(T)$, that

$$E_3(l,l',K,T) = g(T)^{-1}\langle \Psi_1(l,l',K,T) \mid H_1 - E_1 \mid \Psi_1 \rangle \; . \quad (34)$$

This energy increment depends through Ψ_1 on all first-order PW functions $u_1(l,l',K,T)$.

III. COMPUTATIONAL DETAILS

We are concerned with the third-order quantities E_3, $E_3^K(T)$, and $E_3^K(l,l',K,T)$ defined in terms of first-order SAPF's by Eqs. (25a), (29), and (34), respectively. As it has been already mentioned, in this representation these third-order quantities cannot be obtained as sums of contributions determined by individual pairs or individual PW's of a given pair, which is the case for the second-order results. In third order each of these quantities is defined by matrix elements involving the whole first-order wave function, and matrix elements involving different pairs have to be considered. This situation causes a very great increase of the required computer time, which becomes comparable to that needed by a variational calculation within the same basis set. Therefore, we could not afford to use the basis set of 13 880 configurations employed in our second-order calculations for Ne reported in I. Instead, additional work has been invested into the optimization of nonlinear parameters of the radial basis functions $R(u,\eta \mid r)$ defined in I. As a result we obtained an effective set of 20 functions with the parameters specified in Table I. From various subsets of these functions we set up the two-electron radial basis functions used for the expansion of the PW's. The expansion lengths varied in the range from 9 to 64 functions. We considered PW's characterized by $l',l'' \leq 9$. The results reported below were obtained for various subsets of three basis sets which comprise 1358 (set A), 1590 (set B), and 2109 (set C) N-electron configurations. That the qualities of these three basis sets are rather good may be seen from the respective second-order energies which amount to 99.36, 99.49, and 99.64% of the result for the 13 880-configuration case (in our third-order pilot calculation the pertinent characteristic is 88.5%, which, as we shall see, may cause considerable errors).

In the essential part of the present calculations we have used the accurate analytical HF orbitals of Clementi and Roetti[11] spanned by Slater-type orbitals (STO). However, for the stability tests of Sec. IV D less accurate analytical orbitals reported by Huzinaga[12] have also been employed. The linear coefficients of the HF orbitals are slightly modified to fulfill the orthonormalization conditions with double-precision accuracy.

We use extrapolation procedures to remove the inaccuracies of the calculated values due to the limited character of the radial and angular basis sets employed. These procedures can be applied on various levels of the calculations, i.e., on the PW-increment-pair-energy and total-energy levels.

Our radial extrapolation procedure is based on the following observation. We consider basis sets with fixed angular characteristics, i.e., $l_{\max} = \text{const}$, but including varying numbers of radial functions. Let us further assume that these basis sets are flexible enough to yield very good approximations to the second-order quantities considered on the given level of the calculation. For the results obtained within such basis sets we have observed an almost linear dependence between the second- and third-order values considered. To implement our extrapolation procedure we perform on a given level the calculations of the pairs of second- and third-order quantities using subsets of the sets A, B, and C for fixed $l_{\max}$. For the triple of points defined by these pairs we find the straight line by means of the least-squares method with weights assumed to be the reciprocals of the difference between the calculated and exact second-order quantities. We assume that the extrapolated results given in I well represent their exact counterparts. The angular extrapolation on the level of pair and total energies is performed by using an extrapolation parabola determined by five pairs of radially extrapolated second- and third-order values.

The approximate first-order wave function was obtained by the variational-perturbation procedure employing the general computer program developed earlier (see I). The third-order energy contributions were calculated using a new general computer program. This program has been developed based on very concise formulas[13] expressing the energies in terms of radial integrals and 6-j coefficients. The computations were carried out on a RIAD-32 computer in double-precision arithmetics.

IV. THIRD-ORDER ENERGY RESULTS AND DISCUSSION

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

The third-order PW increment to the energy of Kth pair $E_3(l,l',K,T)$ is defined by Eq. (30), which

TABLE II. Third- and second-order PW increments to the pair energies $\bar{E}_i\,(A)=g(T)E_i(A)$, obtained for basis set C (in units of 10^{-6} hartree).

	$1s^2\,{}^1S$		$1s2s\,{}^1S$		$1s2s\,{}^3S$		$2s^2\,{}^1S$				
PW	$i=3$	$i=2$	$i=3$	$i=2$	$i=3$	$i=2$	$i=3$	$i=2$			
ss	−356	−12 114	−40	−1650	−8	−67	29	−3174			
pp	−548	−22 485	−35	−1667	−18	−1238	−120	−1815			
dd	62	−3717	−7	−413	−4	−212	−230	−4609			
ff	38	−1020	0	−107	0	31	−18	−1292			
gg	18	−373	1	−38	0	7	32	−490			
hh	9	−163	1	−16			24	−221			
ii	4	−80	0	−7			15	−112			
jj	2	−43					9	−61			
kk	1	−25					5	−34			
ll	1	−15					3	−21			
	$1s2p\,{}^1P$		$1s2p\,{}^3P$		$2s2p\,{}^1P$		$2s2p\,{}^3P$				
	$i=3$	$i=2$	$i=3$	$i=2$	$i=3$	$i=2$	$i=3$	$i=2$			
sp	−29	−233	2	−6077	−1170	−24 445	2576	−18 122			
pd	−185	−6005	13	−7031	−1073	−12 564	9	−4561			
df	−5	−1210	−1	−595	−1313	−14 479	−353	−3119			
fg	10	−356	2	−97	55	−4525	−2	−577			
gh	6	−139	1	−23	141	−1846	5	−154			
hi	3	−63	0	−6	98	−875	3	−52			
ij	2	−29			61	−462	1	−20			
jk	1	−15			36	−251					
kl	1	−9			24	−158					
	$2p^2\,{}^1S$		$2p^2\,{}^3P$						$2p^2\,{}^1D$		
	$i=3$	$i=2$	$i=3$	$i=2$	$i=3$	$i=2$			PW	$i=3$	$i=2$
ss	−277	−2 280							*sd*	−451	−6669
pp	218	−15 189	5537	−41 212	1133	−40 030			*pf*	−238	−3882
dd	−274	−20 757	−425	−40 356	−879	−23 238			*dg*	−290	−4917
ff	340	−4279	158	−4361	80	−3300			*fh*	114	−1835
gg	200	−1441	77	−907	74	−944			*gi*	95	−826
hh	110	−614	29	−265	44	−368			*hj*	60	−420
ii	62	−301	12	−95	25	−171			*ik*	37	−232
jj	35	−160	6	−39	14	−89			*jl*	23	−137
kk	21	−92	3	−18	8	−48					
ll	13	−56	1	−9	5	−28					

is equivalent to Eq. (34), which, involving only the first-order-type wave functions, provides the basis of the present computations. The results obtained for our most extensive basis set (C) are presented in Table II for all electron pairs of Ne. Values of the second-order PW increments calculated for the same basis sets are also given. For the convenience of presentation we report not directly the PW increments but their values multiplied by $g(T)=g(L,S)$, indicating the number of possible pairs for a given L and S, i.e., we report

$$\bar{E}_i(A)=\bar{E}_i(l,l',K,T)$$

$$=g(T)E_i(l,l',K,T)\quad(i=2,3) \tag{35}$$

where A denotes the set of indices specifying the PW

$$A \leftrightarrow (l,l',K,T)\ . \tag{36}$$

According to Eq. (24) the exact PW increment to the pair energies $E(A)$ can be expanded in terms of consecutive orders of the perturbation theory. Thus, we may consider the quantity

TABLE III. The values of $\bar{E}_i^K$ for the $2p^2\,{}^1S$ pair obtained for various basis sets (in units of 10^{-6} hartree).

$l_{\max}$	i	Basis sets A	 B	 C	Radially[b] extrapolated values
1	3	−569	−568	−566	−563
	2	−17431	−17450	−17469	−17501
2	3	−664	−657	−652	−643
	2	−38157	−38207	−38225	−38278
3	3	−297	−284	−271	−250
	2	−42411	−42475	−42504	−42578
4	3	−50	−22	−4	35
	2	−43826	−43911	−43946	−44047
5	3	136	172	193	244
	2	−44422	−44522	−44559	−44684
6	3	246	287	310	372
	2	−44712	−44820	−44860	−45005
7	3	310	356	379	450
	2	−44866	−44981	−45021	−45183
8	3	349	398	421	499
	2	−44954	−45072	−45113	−45289
9	3	373	424	447	531
	2	−45007	−45129	−45169	−45356
∞[c]	3				63[a]
	2				−4556[a]

[a] Extrapolated results in units of 10^{-5} hartree.

[b] The extrapolated E_2^K values are taken from I.

[c] Extrapolated.

$$E^{(3)}(A)=E_2(A)+E_3(A) \tag{37}$$

as an approximation to $E(A)$ which is expected to be more accurate than $E_2(A)$. The values of $\bar{E}^{(3)}(A)=g(T)E^{(3)}(A)$ can be easily obtained as sums of the neighboring numbers in Table II.

We use the more explicit spectroscopic way to designate electron pairs as well as the letter convention to label the PW's (see I). One can see from the table that, unlike $E_2(A)$, which is always negative, $E_3(A)$ takes both negative and positive values. A common feature of the third-order PW increments is that they are positive for $l,l'>3$, i.e., for high-l indices they bring about a reduction of the absolute values of $E^{(3)}(A)$ if compared with $E_2(A)$. A comparison of the PW increments obtained for the basis sets A, B, and C indicate that for all but the $2p^2\,{}^1D$ and $2p^2\,{}^1S$ pairs the results displayed in Table II, i.e., for basis set C, are very close to the radial limit. For some low-l PW's corresponding to the pairs just mentioned the results in the table may be off by about 5%. The l convergence of the third-order PW's is very fast for the triplet pairs. For the singlet pairs, in turn, this convergence is rather slow. At the present level of accuracy it is still difficult to indicate the precise convergence patterns. It seems, however, that for high-l values the ratio of the consecutive increments tends to a constant value of about 0.6. The l convergence of $E^{(3)}(A)$ is about the same as for $E_2(A)$.

B. Third-order pair energies

The third-order irreducible-pair energies $E_3^K(T)$ are defined by Eq. (26), but we shall base our calculations on the use of Eq. (29). We shall present our pair-energy results as $g(T)$ multiples of $E_i^K(T)$, i.e., in terms of

$$\bar{E}_i^K(T)=g(T)E_i^K(T)\ . \tag{38}$$

We have performed the calculations for the basis sets A, B, and C, and their subsets defined by fixed values of the index $l_{\max}$ that denotes the highest PW taken into account. In this way we have the possibility of studying the convergence both in the

TABLE IV. Calculated[a] and radially extrapolated $\bar{E}_3^K(T)$ energies (in units of 10^{-5} hartree).

	$1s^2\,{}^1S$		$1s2s\,{}^1S$		$1s2s\,{}^3S$		$2s^2\,{}^1S$		$1s2p\,{}^1P$		$1s2p\,{}^3P$	
$l_{\max}$	Calc.[a]	Extr.	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.
1	−112	−112	−9	−9	−6	−6	−20	−20	−4	−4	−6	−6
2	−92	−92	−8	−8	−3	−3	−34	−34	−26	−26	0	0
3	−84	−84	−8	−8	−3	−3	−42	−41	−24	−24	1	1
4	−80	−80	−8	−8	−3	−3	−36	−35	−22	−22	1	2
5	−79	−78	−8	−8			−32	−30	−21	−21	2	2
6	−78	−77	−8	−8			−29	−26	−20	−20	2	2
7	−77	−77					−27	−24	−20	−20		
8	−77	−77					−26	−23	−20	−19		
9	−77	−76					−25	−22	−20	−19		
∞[b]		−76		−8		−3		−20		−19		2

	$2s2p\,{}^1P$		$2s2p\,{}^3P$		$2p^2\,{}^1S$		$2p^2\,{}^1D$		$2p^2\,{}^3P$	
$l_{\max}$	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.	Calc.	Extr.
1	−171	−171	275	275	−57	−56	−1	−1	534	535
2	−303	−303	257	257	−65	−64	−126	−115	512	514
3	−417	−416	221	221	−27	−25	−121	−117	525	527
4	−392	−390	221	221	0	4	−111	−105	530	533
5	−360	−357	223	223	19	24	−72	−64	535	537
6	−340	−336	224	224	31	37	−46	−36	538	540
7	−327	−322	224	224	38	45	−30	−19	539	542
8	−319	−313			42	50	−21	−8	540	542
9	−314	−308			45	53	−15	−2	540	543
∞		−291		225		63		13		544

[a] Results for subsets of C determined by $l_{\max}$.

[b] Extrapolated for $l_{\max} \to \infty$.

radial and angular sense. To get an idea about the convergence characteristics for an individual pair, we present in Table III the results obtained for the $2p^2\,{}^1S$ pair. This pair together with the $2p^2\,{}^1D$ pair disclose the least stability against basis-set modifications. We note from the results of Table III that the values of the third-order pair energies very strongly depend on the accuracy of the first-order wave function both in the radial and angular sense. The dependence on $l_{\max}$ is especially pronounced, e.g., calculations with $l_{\max}=4$ yield E_3^K with the wrong sign. Moreover, the basis-set dependence of E_3^K is much larger than for E_2^K. Let us take, for example, the value obtained for basis set C if $l_{\max}=4$. One can see that the meaningless E_3^K value is associated with the E_2^K result representing 96.4% of the accurate second-order pair energy. The values for $\bar{E}_3^K$, both calculated for various subsets of C ($l_{\max}=\text{const}$) and extrapolated (on the pair-energy level) according to the procedures described in Sec. III, are listed in Table IV. These values exhibit different stabilities with respect to the basis-set incompleteness. We note that for the triplet pairs the results little depend on the completeness of the basis sets used. For the singlet pairs this dependence is much stronger, and even critical in some cases, e.g., for the $2p^2\,{}^1S$ and $2p^2\,{}^1D$ pairs.

To get an idea about both the reliability of the extrapolation procedures used and the accuracies of the extrapolated $\bar{E}_3^K(T)$ values we performed also the extrapolation of $\bar{E}_3^K(T)$ in a different way which is described in Appendix D. The results are practically identical to those displayed in Table IV for all but the $2p^2\,{}^1D$ pair. The $E_3(T)$ results for the pair just mentioned, which is the most sensitive to the structure of the basis set, are discussed in Appendix D. The alternative extrapolation yields the value of 0.000 11 hartree, which is in satisfactory agreement with the value of 0.000 13 hartree displayed in Table V.

To get an idea about the relative values of the second- and third-order pair energies we collected, in Table V, the pertinent calculated and extrapolated values. We also show the extrapolated results for $\bar{E}_2^K+\bar{E}_3^K$ which represent an approximation to

TABLE V. Pair energies for Ne (in units of 10^{-5} hartree).

Pair	E_2^K Calc.[a]	E_2^K Extr.[b]	E_3^K Calc.	E_3^K Extr.[c]	$E_2^K+E_3^K$ Extr.
$1s^2\ {}^1S$	−4003	−4022	−77	−76	−4098
$1s2s\ {}^1S$	−390	−397	−8	−8	−405
$1s2s\ {}^3S$	−156	−159	−3	−3	−162
$2s^2\ {}^1S$	−1183	−1202	−25	−20	−1222
$1s2p\ {}^1P$	−806	−813	−20	−19	−832
$1s2p\ {}^3P$	−1383	−1404	1	2	−1402
$2s2p\ {}^1P$	−5961	−6033	−314	−291	−6324
$2s2p\ {}^3P$	−2661	−2682	224	225	−2457
$2p^2\ {}^1S$	−4517	−4556	45	63	−4493
$2p^2\ {}^1D$	−8713	−8785	−15	13	−8772
$2p^2\ {}^3P$	−8726	−8739	540	544	−8195
Third-order energy, E_3			0.003 49[d]	0.004 30[d]	

[a] Using basis set C, $1_{\max}=9$.
[b] Quoted from I.
[c] Radial and angular extrapolation.
[d] In hartrees.

the $g(T)$ multiple of the exact energies defined by Eq. (13). One can see that the modification caused by the third-order values is smaller than for the PW increments (Table II). In most cases, the changes are of the order of 2%. Only for the $2s2p\ {}^3P$, $2p^2\ {}^3P$, and $2s2p\ {}^1P$ pairs the changes amount to 8, 6, and 5%, respectively. It may be interesting to note that the modifications of E_2^K by E_3^K are, in the case of the nsn's pairs, much smaller for Ne than for Be.[14] In the former case they amount to 1.9, 2.0, and 0.7% for the configurational pairs $1s^2$, $1s2s$, and $2s^2$, respectively. For Be, in turn, the corresponding values are 5, 14, and 25%. This different behavior is apparently caused by the quasidegeneracy of the Be ground state.

We display also in Table VI some of the configurational-pair energies defined as

$$\bar{E}_3^K = \sum_T g(T) E_3^{K\prime} T) \ . \tag{39}$$

The results are obtained by using the extrapolation procedure given in Sec. III (on the level of configurational-pair energies). A comparison of the results of this extrapolation with the values obtained by taking sums of extrapolated pair energies (from Table IV) discloses an agreement within the

TABLE VI. Radially extrapolated third-order configurational-pair energies $\bar{E}_3^K$ (in units of 10^{-6} hartree).

Pair	$l_{\max}$	This[a] work	Lindgren Salomonson[b]	Pair	$l_{\max}$	This work	Lindgren Salomonson
$1s^2$	4	−799	−794	$1s2p$	4	−203	−204
	7	−766			7	−176	
	9	−763			9	−172	
$1s2s$	4	−110	−104	$2s2p$	4	−1683	−1293
	7	−108			7	−974	−973
	9				9	−831	
$2s^2$	4	−350	−319	$2p^2$	4	4302	5419
	7	−244			7	5680	5951
	9	−224			9	5952	

[a] Radially extrapolated on the E^K level.
[b] Reference 8.

TABLE VII. Second- and third-order energies for Ne (in units of 10^{-5} hartree).

	Calculated[b]		Radially extrapolated	
$l_{\max}$	E_3	E_2	E_3	E_2
1	423	$-19\,180$	425	$-19\,204$
2	111	$-32\,193$	117	$-32\,238$
3	20	$-35\,961$	30	$-36\,027$
4	100	$-37\,428$	116	$-37\,512$
5	205	$-37\,992$	227	$-38\,092$
6	271	$-38\,251$	298	$-38\,363$
7	311	$-38\,383$	343	$-38\,507$
8	334	$-38\,455$	370	$-38\,588$
9	349	$-38\,498$	387	$-38\,638$
∞[d]				
			0.0044[a]	-0.3879[a,c]

[a] In hartrees.
[b] For basis set C.
[c] Quoted from I.
[d] Extrapolated.

limits of $\pm 0.000\,01$ hartree. This agreement supports our expectation about the reliability of our extrapolation procedures. The E_3^K values can be compared with the results obtained by Lindgren and Salomonson[8] within their procedure involving also radial extrapolation. One can see from Table VI that the two sets of results disclose a satisfactory agreement, which distinctively improves when proceeding to higher $l_{\max}$ values.

C. Third-order energies

Having calculated all $E_3^K(T)$ or E_3^K energies one can readily obtain E_3. For the basis sets A, B, and C ($l_{\max}=9$) we have obtained for E_3 the values of 0.003 19, 0.003 35, and 0.003 49 hartree, respectively. These results correspond to the second-order values of $-0.383\,88$, $-0.384\,37$, and $-0.384\,97$ hartree, respectively. We see again that the basis-set dependence of E_3 is much larger than for E_2. In Table VII we display for various $l_{\max}$ the values of E_3 calculated and extrapolated on the level of total energies according to Sec. III. The pertinent E_2 values are also shown in this table. The results for E_3 exhibit the strong $l_{\max}$ dependence which was already found on the pair-energy level. For example, we note from the table that taking subsets of basis set C for $l_{\max}=3$ and 4 one obtains 6 and 29% of the result for $l_{\max}=9$, respectively. For E_2 we would obtain 93 and 97% of the result for $l_{\max}=9$. Basing on the Hylleraas variational principle,[10] one can consider the value of E_2 as an energy criterion of the accuracy of Ψ_1. Hence, one can see that for obtaining reliable E_3 results one has to take very accurate first-order functions. To visualize the fact that the accuracy requirements for Ψ_1 are really critical, let us mention that for a function yielding 92% of E_2 we have obtained a negative E_3 value. Let us now consider both the radially and angularly extrapolated E_3 energies. The value obtained as a result of adding the extrapolated pair energies (see Table V) amounts to 0.0043 hartree, which compares well with the value of 0.0044 hartree obtained when extrapolating on the total-energy level (see Table VII). The agreement of the results of the different extrapolation procedures seems to indicate that the third-order energy for the ground state of Ne takes the value $E_3=0.0044\pm0.0002$ hartree.

The E_3 energy can also be written as a sum of the contributions

$$E_3^{KK',TT'}=\langle \Psi_1(K,T)\,|\,H_1-E_1\,|\,\Psi_1(K',T')\rangle\ , \tag{40}$$

which are defined in terms of the first-order wave functions $u_1^K(T\,|\,2)$ and $u_1^{K'}(T'\,|\,2)$. In I we have discussed the relative magnitudes of the diagonal ($K=K'$ and $T=T'$) and off-diagonal contributions and found that for pairs involving $2p$ electrons these contributions are of equal importance. To visualize this fact let us mention that for the $2p^2\,{}^3P$ and $2p^2\,{}^1D$ pairs the diagonal contributions calculated in basis C are $-0.007\,07$ and $-0.006\,87$ hartree, respectively, whereas the off-diagonal contribution amounts to 0.014 91 hartree. To get a general idea about the relative magnitude of contributions to E_3 from different subshells we display in Table VIII the values of

$$E_3^{K,K'}=\sum_{T,T'} E_3^{KK',TT'} \tag{41}$$

TABLE VIII. The diagonal and off-diagonal configurational-pair contributions $E_3^{K,K'}$ for Ne (in units of 10^{-6} hartree).

K K'	$1s^2$	$1s\,2s$	$2s^2$	$1s\,2p$	$2s\,2p$	$2p^2$
$1s^2$	-845					
$1s\,2s$	-23	-149				
$2s^2$	16	-6	-353			
$1s\,2p$	129	14	0	-667		
$2s\,2p$	0	71	-1169	75	-871	
$2p^2$	31	24	1364	757	967	4129

TABLE IX. Radially extrapolated E_3 and E_2 values for various HF orbitals (in units of 10^{-5} hartree).

	$(4s,2p)$ STO basis ($E_{\mathrm{HF}}=-128.53508$ hartree)[a]		$(4s,3p)$ STO basis ($E_{\mathrm{HF}}=-128.54648$ hartree)[b]		$(6s,4p)$ STO basis ($E_{\mathrm{HF}}=-128.54705$ hartree)[b]	
$l_{\max}$	E_2	E_3	E_2	E_3	E_2	E_3
1	−19083	365	−19188	420	−19204	425
2	−32136	56	−32224	113	−32238	117
3	−35931	−31	−36014	25	−36027	30
4	−37420	54	−37499	111	−37512	116
5	−38002	166	−38079	222	−38092	227
6	−38274	237	−38350	293	−38363	298
7	−38418	282	−38494	338	−38507	343
8	−38499	310	−38575	365	−38588	370
9	−38549	327	−38625	382	−38638	387
∞[d]	−3870[c]	38[c]	−3878[c]	44[c]	−3879[a,c]	44[c]

[a] Reference 11.
[b] Reference 12.
[c] Units of 10^{-4} hartree.
[d] Extrapolated.

calculated for the basis set *C*. One can see that only for the nsn's pairs the off-diagonal contributions are small in comparison with the diagonal ones. Such a situation was also found by Byron and Joachain[14] for Be.

D. The effect of the accuracy of the HF orbitals on E_3

The derivation of all the second- and third-order expressions is based on the assumption that we have an accurate solution to the HF equations. The problem for the second-order energy was already discussed by Pan and King,[15] who found that a meaningful calculation does not require extremely accurate HF orbitals. Let us now consider the problem of the impact of the approximate character of the HF orbitals on the value of the third-order energy which, as we have seen, is very sensitive to the accuracy of Ψ_1. We have performed numerical experiments in which the quality of the HF orbitals is varied. We have repeated all the calculations discussed in Secs. IV A – IV C for two sets of HF orbitals which are of lower accuracy. These orbitals were obtained by Huzinaga[12] within $(4s,2p)$ and $(4s,3p)$ STO basis sets. The pertinent HF energies are given in the upper part of Table IX. The problem of the relative quality of the orbital sets may be answered using the energy criterion, i.e., by a comparison of E_{HF} for each case with the very accurate E_{HF}^{n} energy obtained by solving numerically the HF equations. For this energy we have obtained the result $E_{\mathrm{HF}}^{n}=-128.547098$ using Froese-Fischer's[16] HF program. Taking the E_{HF} values from Table IX one can see that the three orbital sets may be characterized by the following values of the energy differences $E_{\mathrm{HF}}-E_{\mathrm{HF}}^{n}$: 0.01202, 0.00062, and 0.00005 hartree. The latter value indicates that the Clementi-Roetti HF orbitals are almost identical with the numerical ones. This conclusion may be further supported by comparison of the corresponding orbital energies obtained in both cases. When changing the set of HF orbitals the results are modified in a rather regular way on all levels of the calculations. This behavior is well characterized by the results for the radially extrapolated E_3 values displayed in Table IX for the three sets of HF orbitals considered. The last two columns corresponding to the Clementi-Roetti orbitals are taken from Table VII. As may be seen in Table IX, the results for E_3 obtained when using the three sets of HF orbitals disclose the most pronounced difference for low $l_{\max}$ values. For $l_{\max}=9$ the difference of the $(4s,2p)$ and $(6s,4p)$ results amounts to 16%, whereas the difference of the corresponding $(4s,3p)$ and $(6s,4p)$ values is of about 1.3%. The corresponding differences for the E_2 values are much smaller amounting to 0.2 and 0.03%, respectively, which is a confirmation of the finding of Pan and King. One can also see from the table that the extrapolated E_3 energies are identical for the $(4s,3p)$ and $(6s,4p)$ orbital sets. Since the third-order results are almost identical for the $(4s,3p)$ and $(6s,4p)$ HF orbitals which lead

TABLE X. Comparsion of the third-order energy of Ne (in hartrees).

Authors and method	$l_{\max}$	E_3	E_2
Pople *et al.* (Ref. 21)	2	−0.000 48	−0.254 52
Urban *et al.* (Ref. 18)	2	0.001 18	−0.215 66
Wilson and Silver (Ref. 17)	2	0.000 72	−0.250 52
Lindgren and Salomonson (Refs. 7 and 8)—radially extrapolated	6−8	0.003 5	−0.3883[b]
This work:			
calculated (basis set *C*)	9	0.003 49	−0.384 97
Radially extrapolated	2	0.001 17	−0.322 38
	7	0.003 43	−0.385 07
	9	0.003 87	−0.386 38
Radially and angularly Extrapolated	∞	0.0044±0.0002	−0.3879[a]

[a] Quoted from I.

[b] Radially and angularly extrpolated result.

to E_{HF} values differing by $-0.000\,57$ hartree, we may expect that these results will also be identical when comparing the $(6s,4p)$ and numerical HF orbitals, for which the difference of E_{HF} amounts to $-0.000\,05$ hartree. Hence, our numerical experiment leads us to a conclusion that our third-order results are not affected by the approximate character of the Clementi-Roetti orbitals.

E. Comparison with other work

We know only about a few attempts of evaluating the third-order energy for Ne. Except I and the work of Lindgren and Salomonson,[7,8] the E_3 values were obtained from calculations within very limited basis sets. We collect in Table X the values obtained by various workers. The results in the first three rows were obtained for first-order wave functions yielding E_2 representing 55−66 % of the exact E_2 result. As we have demonstrated above, for such inaccurate first-order functions the E_3 values have very little in common with the exact third-order energy defined within the Rayleigh-Schrödinger perturbation theory for the N-electron problem. Therefore, the E_3 values obtained at such a low level of accuracy should be considered only as third-order corrections for some model problems defined, e.g., by a given basis set, which is, in fact, the case for the algebraic approximation to MBPT developed by Wilson and Silver.[17] The work of Lindgren and Salomonson is based on calculations including PW's up to $l_{\max}=7$ (for off-diagonal PW's up to $l'_{\max}+l''_{\max}=14$). The procedure includes radial but not angular extrapolation. One can see from Table X that their value of 0.0035 hartree is in excellent agreement with our value for $l_{\max}=7$.

V. SUMMARY

We have expressed the exact correlation energy in terms of exact symmetry-adapted pair energies and exact PW increments to these pair energies. Next, all these quantities are represented in terms of perturbative contributions within the Rayleigh-Schrödinger approach based on $H_0=H_{\mathrm{HF}}$. The main attention has been paid to the third-order contributions which are expressible in terms of first-order SAPF's and first-order PW's. These functions have been determined by the method developed in I, and are employed in the evaluation of the third-order PW increments, $E_3(A)$, third-order pair energies $E_3^K(T)$, and the total third-order energy E_3. It turned out that all these values are very sensitive to the accuracies of the first-order pair functions, i.e., to the completeness of the basis sets used. This basis-set dependence is much stronger than for the second-order energies. We have used basis sets that are extensive in size (up to $l_{\max}=9$) and are flexible enough to yield reliable results. Nevertheless, our values required extrapolations both in the radial and angular sense. We have employed independent extrapolation procedures on all four different levels of the calculations. The results obtained by various extrapolation procedures disclosed satisfactory agreement. We have obtained the extrapolated value of $E_3 = 0.0044 \pm 0.0002$ hartree, which represents 1.1% of the E_2 energy. The values of the individual second-order PW increments and pair energies are in some cases modified by about 10%. However, those modifications cancel to a significant degree leading to the small change of E_2. We have also found that the off-diagonal and diagonal contributions to E_3 are of the same order of magnitude, which precludes the application of independent-pair-like approaches to the evaluation of E_3. Since the determination of reliable E_3 values requires Ψ_1 functions of very high accuracy (yielding for Ne 99% of the exact E_2), most of the E_3 energies recently obtained in various small-basis-set calculations have little in common with the third-order energy for the real N-electron problem. The same may be true for the E_4 values recently computed for very limited basis sets (see, e.g., Refs. 18 and 19). The lack of reliable information about the structure of E_4 hinders the full understanding of the pair-pair coupling effects, which are crucial in accurate many-electron theories. Therefore, in the future more effort has to be paid to the accurate evaluation of E_4 for systems of the size comparable to Ne. We found in our calculations that for two first-order functions that are not of high accuracy it is possible to get the same E_2 value and two E_3 values of different sign. This situation must raise some questions about the purposefulness of using the [2/1] Padé approximants (or even the $[n+1/n]$ ones) to get more accurate approximations to the correlation energy than in the perturbation theory through the $(2n+1)$st order (see, e.g., Ref. 17). The unstable behavior of E_3 (and perhaps E_4) may suggest that one should carefully consider for a given system whether it is more worthwhile to perform higher-order MBPT calculations within a very limited basis set than to calculate just E_2, but within a more extensive basis set. The latter is certainly the proper approach for Ne.

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APPENDIX A: SYMMETRY-ADAPTED FORM OF FUNCTIONS BELONGING TO THE SUBSPACE SPANNED BY DOUBLY EXCITED CONFIGURATIONS

Let K denote a configurational pair of orbitals belonging to the subshells of equivalent orbitals $n_i l_i$ and $n_j l_j$, i.e., $K \equiv (n_i l_i, n_j l_j)$. If $i \neq j$ and $i = j$, we have the inter- and intrashell case of I, respectively. Before proceeding further let us consider the HF reference function Ψ_0 for the closed-shell $(\bar{L} = \bar{S} = 0)$ ground state of the N-electron atom. For each pair of occupied orbitals K one can rewrite Ψ_0 (defined as in I) in the following form:

$$\Psi_0 = \sum_T a_T^K \{ \Phi_0^K(T \mid N-2) u_0^K(T \mid 2) \} , \qquad \text{(A1)}$$

where $\Phi_0^K(T \mid N-2)$ is a normalized antisymmetric function characterized by the $T = (L,S)$ eigenvalues of the angular momenta operators. The electron configuration involved differs from the configuration of Ψ_0 by removing the configurational pair K. The one-electron functions of this pair are coupled, giving rise to the pair function $u_0^K(T \mid 2)$. The braces denote that we take a vector-coupled product corresponding to $\bar{L} = \bar{S} = 0$. One can see from I (Sec. II A 1 – II A 5) that for intrashell pairs a_T^K is just the two-electron coefficient of fractional parentage[20] for the shell defined by $K \equiv (nl, nl)$. For closed parent shells this coefficient is of the form

$$a_T^K = a_{LS}^K$$

$$= [(2l+1)(2S+1)]^{1/2} \begin{bmatrix} 4l+2 \\ 2 \end{bmatrix}^{-1/2} . \qquad \text{(A2)}$$

For intershell pairs, $K \equiv (n_i l_i, n_j l_j)$, one can see from (5e) of I that

$$a_T^K = a_{LS}^K = \left[\frac{(2L+1)(2S+1)}{(4l_i+2)(4l_j+2)} \right]^{1/2} . \qquad \text{(A3)}$$

Let us consider the set of antisymmetric N-electron functions, designated by $\bar{L} = \bar{S} = 0$, which are obtainable from the reference function Ψ_0 by double excitations from the given Kth orbital pair to any pair of virtual orbitals orthogonal to the occupied orbitals. Then, using the possibility of representing Ψ_0 in the symmetry-adapted form (A1) for the given pair K, one can easily cast every function belonging to the subspace spanned by this set into the symmetry-adapted form

$$\chi_i^K = \mathscr{A}^K \sum_T a_T^K \{ \Phi_0^K(T \mid N-2) u_i^K(T \mid 2) \} , \tag{A4}$$

where $\mathscr{A}^K$ denotes an antisymmetrizer which must be introduced to ensure the antisymmetry of χ_i^K. Since the virtual orbitals are orthogonal to the occupied ones the antisymmetric pair function $u_i^K(T \mid 2)$ is strongly orthogonal to all ground-state orbitals, and consequently to the functions Φ_0^K and u_0^K.

Finally, if one takes a basis set being a union over all possible pairs K of the basis sets defined above, then any function belonging to the subspace spanned by this basis set can be written in the symmetry-adapted form

$$\chi_i = \sum_K a^K \sum_T a_T^K \{ \Phi_0^K(T \mid N-2) u_i^K(T \mid 2) \} . \tag{A5}$$

APPENDIX B: CORRELATION ENERGY IN TERMS OF PAIR-CORRELATION ENERGIES AND PW INCREMENTS

Let E_{corr}^i be a contribution to the correlation energy determined by the function χ_i belonging to the subspace of all doubly excited configurations:

$$E_{\mathrm{corr},i} = \langle \Psi_0 \mid H_1 \mid \chi_i \rangle . \tag{B1}$$

We assume that H_1 can be represented as a two-particle operator

$$H_1 = \sum_{i<j} g_{ij} . \tag{B2}$$

Inserting the functions (A1) and (A5) into Eq. (B1) we obtain

$$\langle \Psi_0 \mid H_1 \mid \chi_i \rangle = \sum_{K,K'} \sum_{T,T'} a_T^K a_{T'}^{K'} \langle \{ \Phi_0^K(T \mid N-2) u_0^K(T \mid 2) \} \mid H_1 \mid \mathscr{A}^{K'} \{ \Phi_0^{K'}(T' \mid N-2) u_i^{K'}(T' \mid 2) \} \rangle . \tag{B3}$$

Since the product of the bra function and the H_1 operator is antisymmetric with respect to the permutations of electrons involved in $\mathscr{A}^{K'}$, we can eliminate the antisymmetrizer from the matrix element on the right-hand side of Eq. (B3) and obtain for this matrix element the result

$$b^{K'} \langle \{ \Phi_0^K(T \mid N-2) u_0^K(T \mid 2) \} \mid H_1 \mid \{ \Phi_0^{K'}(T' \mid N-2) u_i^{K'}(T' \mid 2) \} \rangle , \tag{B4}$$

where $b^{K'}$ indicates the number of permutations involved in $\mathscr{A}^K$. This number depends on the configuration-pair K considered and amounts to

$$b^K = \begin{cases} \begin{bmatrix} 4l+2 \\ 2 \end{bmatrix} & \text{for } K = (nl,nl) \\ (4l+2)(4l'+2) & \text{for } K + (nl,n'l') . \end{cases} \tag{B5}$$

We assume that the pair functions u_0 and u_i pertain to the $(N-1)$- and Nth electrons. Taking into account the strong orthogonality of u_i^K both to Φ_0^K and u_0^K as well as the orthogonality condition $\langle \Phi_0^K(T) \mid \Phi_0^{K'}(T) \rangle = \delta_{KK'} \delta_{TT'}$, Eq. (B4) can be reexpressed as

$$b^{K'} \langle \{ \Phi_0^K(T \mid N-2) u_0^K(T \mid 2) \} \mid g_{N-1,N} \mid \{ \Phi_0^{K'}(T \mid N-2) u_i^{K'}(T \mid 2) \} \rangle$$
$$= b^{K'} \delta_{TT'} \delta_{KK'} \langle u_0^K(T \mid 2) \mid g \mid u_i^K(T \mid 2) \rangle . \tag{B6}$$

Inserting this result into (B3), and taking into account (A2), (A3), and (B5) one obtains

$$\begin{aligned} \langle \Psi_0 \mid H_1 \mid \chi_i \rangle &= \sum_K \sum_T (a_T^K)^2 b^K \langle u_0^K(T \mid 2) \mid g \mid u_i^K(T \mid 2) \rangle \\ &= \sum_K \sum_T g(T) \langle u_0^K(T \mid 2) \mid g \mid u_i^K(T \mid 2) \rangle . \end{aligned}$$

We can therefore write

$$E_{\mathrm{corr},i}=\sum_{K}\sum_{T} g(T)E_i^K(T)\ , \tag{B7}$$

with

$$E_i^K(T)=\langle u_0^K(T\mid 2)\mid g\mid u_i^K(T\mid 2)\rangle \tag{B8}$$

representing the correlation energy of the Kth pair determined by the SAPF u_i^K.

It is often convenient to define the SAPF's in terms of partial-wave (PW) expansion (see, e.g., Sec. II in I)

$$u_i^K(T\mid 2)=\sum_{l,l'} u_i(l,l',K,T\mid x_1,x_2) \tag{B9}$$

with (T stands for L and S)

$$\begin{aligned} u_i(l,l',K,T\mid x_1,x_2) &= \mathscr{B}R^{K,T}_{ll',i}(r_1,r_2)Z^{(l,l')}(L,M_L\mid\delta_1,\delta_2)\\ &\quad\times\mathscr{S}(S,M_S\mid\sigma_1,\sigma_2)\ , \end{aligned} \tag{B10}$$

where $\mathscr{B}$ is a two-particle antisymmetrizer and the functions $Z^{(l,l')}$ and $\mathscr{S}$ have been defined in I. The correlation energy of the pair can be reexpressed in the form

$$E_i^K(T)=\sum_{l,l'} E_i(l,l',K,T)\ , \tag{B11}$$

where the PW increments to the pair energy are defined as

$$\begin{aligned} &E_i(l,l',K,T)\\ &\quad=\langle u_0^K(T\mid 2)\mid g\mid u_i(l,l',K,T)\rangle\ . \end{aligned} \tag{B12}$$

APPENDIX C: THIRD-ORDER PAIR ENERGY

The first- and second-order wave functions fulfill the following equations[10]:

$$(H_0-E_0)\Psi_1+(H_1-E_1)\Psi_0=0\ , \tag{C1}$$

$$(H_0-E_0)\Psi_2+(H_1-E_1)\Psi_1+E_0\Psi_2=0\ . \tag{C2a}$$

For our aim it is sufficient to know the function $\Phi_2=P^{(2)}\Psi_2$ which satisfies the equation

$$(H_0-E_0)\Phi_2+P^{(2)}(H_1-E_1)\Psi_1=0\ , \tag{C2b}$$

obtained by acting with the projector $P^{(2)}$ on (C2a). Writing Ψ_0 and Ψ_1 in the forms (A1) and (A5), respectively, and inserting into Eq. (18) one can find the following equation satisfied by the first-order function $u_1^K(T\mid 2)$:

$$\begin{aligned} &[h^{(2)}(N-1,N)-E_0^K]u_1^K(T\mid 2)\\ &\qquad+[g_{N-1,N}-E_1^K(T)]u_0^K(T\mid 2)=0\ , \end{aligned} \tag{C3}$$

where $(N-1)$ and N denote the variables of the pair function,

$$h^{(2)}(N-1,N)\equiv h(N-1)+h(N)\ ,$$

and E_0^K is the sum of HF orbital energies corresponding to the electrons of the Kth pair. Multiplying (C3) to the left by $u_2(L,S\mid 2)$ and taking the complex conjugate of the scalar product, one obtains

$$\begin{aligned} E_3^K(T)&=\langle u_0^K(T\mid 2)\mid g\mid u_2^K(T\mid 2)\rangle\\ &=-\langle u_1^K(T\mid 2)\mid h^{(2)}-E_0^K\mid u_2^K(T\mid 2)\rangle\ . \end{aligned} \tag{C4}$$

Let us now, using Eq. (A5), express Φ_2 in terms of second-order pair functions $u_2(L,S\mid 2)$ and insert into (C2b). Next, we evaluate the scalar product of the left-hand side of Eq. (C2b) with the function $\Psi_1(K,T)$ defined by Eq. (28). We obtain for the first term

$$\begin{aligned} &a_T^K\langle \mathscr{A}^K\{\Phi_0^K(T\mid N-2)u_1^K(T\mid 2)\}\mid H_0-E_0\mid\Phi_2\rangle\\ &\quad=(a_T^K)^2b^K\\ &\qquad\times\langle u_1^K(T\mid 2)\mid h^{(2)}-E_0^K\mid u_2^K(T\mid 2)\rangle\\ &\quad=g(T)\langle u_1^K(T\mid 2)\mid h^{(2)}-E_0^K\mid u_2(T\mid 2)\rangle\ , \end{aligned} \tag{C5}$$

where $g(T)$ and b^K are defined by Eqs. (12) and (B5), respectively. For the second term we obtain

$$\begin{aligned} &\langle\Psi_1(K;T)\mid P_2(H_1-E_1)\mid\Psi_1\rangle\\ &\qquad=\langle\Psi_1(K;T)\mid H_1-E_1)\mid\Psi_1\rangle\ . \end{aligned} \tag{C6}$$

We have, hence,

$$\begin{aligned} &g(T)\langle u_1^K(T\mid 2)\mid h^{(2)}-E_0^K\mid u_2(T\mid 2)\\ &\qquad=-\langle\Psi_1(K;T)\mid H_1-E_1\mid\Psi_1\rangle\ . \end{aligned} \tag{C7}$$

Combining (C7) with (C4) one obtains

$$E_3^K(T)=g(T)^{-1}\langle\Psi_1(K,T)\mid H_1-E_1\mid\Psi_1\rangle\ ,$$

which is the desired representation for E_3^K in terms of matrix elements involving the first-order SAPF's.

TABLE XI. Radially and angularly extrapolated PW increments, $\bar{E}_3(A)$ for the pair $2p^2\,{}^1D$ (in units of 10^{-6} hartree).

PW	Calc. (basis C)	Rad. extr. ($l_{\max}=9$)	Rad. and ang. extr.	PW	Calc. (basis C)	Rad. extr. ($l_{\max}=9$)	Rad. and ang. extr.
pp	1133	1149	1160	*sd*	−451	−441	−437
dd	−879	−871	−858	*pf*	−238	−218	−211
ff	80	88	93	*dg*	−290	−283	−275
gg	74	79	81	*fh*	114	121	126
hh	44	47	49	*gi*	95	101	106
ii	25	27	28	*hj*	60	67	70
jj	14	17	18	*ik*	37	42	45
kk	8	10	10	*jl*	23	26	29
ll	5	7	7	$l',l''>g$			54
$l'>9$			11				
Third-order pair energy for $2p^2\,{}^1D$					−146	−32	105

APPENDIX D: ALTERNATIVE EXTRAPOLATION PROCEDURE FOR E_3^K

As one can see from Eq. (34) the third-order PW increments to the pair energies

$$E_3(A)\equiv E_3(l,l',K,T)$$

depend through Ψ_1 on all PW's of the system, i.e., the value of each $E_3(A)$ depends on $l_{\max}$. Therefore, to get accurate $E_3(A)$ values one has to perform extrapolations both in the radial and angular sense. Basing on the results of our computations for various subsets of the basis sets *A*, *B*, and *C* we can attempt such extrapolations. In Table XI we present the result for the $2p^2\,{}^1D$ pair for which (see Table IV) the pair energy discloses the greatest sensibility to the completeness of the basis sets. The radially extrapolated $\bar{E}_3(A)$ values were obtained from the extrapolations of the results for basis sets *A*, *B*, and *C* ($l_{\max}=9$) by means of the procedure described in Sec. III (on the PW level). Such extrapolation procedures were also performed for all $l_{\max}<9$ providing for each PW a sequence of *l*-dependent values. These values disclosed an $l^{-4,3}$ behavior for the diagonal PW's and an l^{-5} behavior for the nondiagonal ones. Taking into account these convergence patterns we obtained the radially and angularly extrapolated values shown in the table. The sum of the PW increments for $l,l'>9$ is approximated basing on the fact that for high *l* indices the PW increments behave like members of a geometric series. Taking a sum of the $\bar{E}_3(A)$ values we obtain the third-order pair energies displayed in the lowest row of Table XI.

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