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Many-Body Perturbation-Theory Calculations with Finite, Bound Basis Sets

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The feasibility of many-body perturbation-theory (MBPT) calculations with hole and particle states expanded in a finite set of bound-type functions is investigated. The correlation energy of atomic beryllium is used as a test case. Particle states with negative and positive energy values are treated uniformly. We find that convergence of individual diagrams to better than 10^{-4} a.u., and similar agreement with Kelly's numerical results can be obtained using basis sets composed of 9*s*, 7*p*, 5*d*, and 4*f* Slater orbitals for intrashell correlation and a 10*s* 8*p* 6*d* 4*f* set for the intershell effects. The total correlation energy calculated with these basis functions is in good agreement with experiment. These results indicate that MBPT calculations by the expansion method are indeed feasible. While this method may not be more convenient than the numerical approach for atomic systems, it should be useful for molecular calculations, where finding a suitable complete set of numerical orbitals presents difficult problems.

I. INTRODUCTION

The many-body perturbation theory (MBPT) of Brueckner[1] and Goldstone[2] was first applied to atomic systems by Kelly.[3] The method has proved very useful and numerous calculations of correlation energies and other atomic properties have been carried out by Kelly[4] and others.[5] The complete basis sets needed for diagram evaluation were obtained in numerical form as eigenfunctions of an appropriate Hartree–Fock operator serving as a zero-order Hamiltonian, and included bound- and continuum-type functions. The MBPT method has recently been applied to molecules,[6,7] where finding a complete basis set presents a more difficult problem. H_2^+ orbitals in eliptic coordinates were used in the H_2 calculation of Dutta *et al.*[7(b)]; in the other cases quoted (H_2,[6(a),6(b)] H_2O,[6(c)] and HF[7(a)]) a one-center operator was employed to generate the basis orbitals. This choice of a zero-order Hamiltonian leaves a rather large perturbation and makes it necessary to calculate difficult high-order diagrams. Corrections due to the hydrogen nuclei heavily outweigh usual correlation effects even for H_2O[6(c)] and HF,[7(a)] and it would seem hopeless to apply the method to molecules with more than one "heavy" atom (heavier than hydrogen). The expansion method used extensively in atomic and molecular calculations, whereby orbitals are expanded in a finite set of analytical functions centered about the different nuclei, may provide a solution to the problem. The discrete orbital energy spectrum obtained by the expansion method includes, in general, both negative and positive values, and this approach to MBPT calculations will have the advantage of treating bound and continuum states on equal footing and avoiding cumbersome integrations over continuum states.

The basis functions commonly used in atomic and molecular calculations, such as Slater or Gaussian orbitals, decay at infinity and are square integrable, whereas the positive-energy orbitals used in numerical MBPT work satisfy oscillatory boundary conditions. Basis sets consisting of bound-type[8] functions only are routinely used for evaluating correlation energies and other properties by various methods (e.g., configuration interaction), and they may be applicable to MBPT calculations too. An attempt in this direction has been reported by Schulman and Kaufman.[9] They calculated the correlation energy, polarizabilities, and electron-coupled nuclear spin-spin interaction in the hydrogen molecule with a basis set consisting of 10*s*, 5*p*, and 1*d* Gaussian functions on each atom, and obtained reasonably good agreement with experiment. Only diagrams of low order (up to second order for the energy, first order for the other properties) have been evaluated by Schulman and Kaufman,[9] and no equivalent work with numerical orbitals is available for comparison. Further tests of the feasibility of MBPT calculations by the expansion method seem to be called for before it can be widely implemented. The beryllium atom provides a useful test case, since detailed results obtained by the numerical MBPT method are available.[3,10]

The adequacy of finite bound-type basis sets for a MBPT calculation of the correlation energy of Be is tested below in several ways. First, the convergence of individual diagrams with respect to the basis set is investigated (Sec. II B); next, the converged results are compared with Kelly's values[3,10] obtained with numerical orbitals (Sec. III); finally, an additional test is provided by calculating the total correlation energy of the atom and the contributions of the separate electron pairs and triples to it and comparing them with available experimental and theoretical results (Sec. IV). Section V includes the conclusions drawn from the calculations.

II. ONE-ELECTRON STATES

A. Zero-Order Hamiltonian

The Hamiltonian of a general N-electron system is

$$H=\sum_{i=1}^{N} h_i+\sum_{i>j} v_{ij} , \tag{1}$$

where h_i is the one-electron part and v_{ij} is the electron-electron repulsion. This repulsion may be approximated by a one-electron operator V, and a zero-order Hamiltonian

$$H_0=\sum_{i=1}^{N} (h_i+V_i) \tag{2}$$

is then written, with zero-order functions and energies satisfying

$$H_0\Phi_0=E_0\Phi_0 . \tag{3}$$

The perturbing operator is

$$H'=H-H_0=\sum_{i>j}^{N} v_{ij}-\sum_{i=1}^{N} V_i , \tag{4}$$

and terms in the perturbation series are calculated with the help of a complete set of orbitals φ_n obtained from

$$(h+V)\varphi_n=\epsilon_n\varphi_n . \tag{5}$$

The choice of V affects the convergence of the perturbation series. Kelly[3] first used the potential

$$V^N=\sum_{i=1}^{N} (J_i-K_i) , \tag{6}$$

where J_i and K_i are the usual Coulomb and exchange operators, respectively. Equation (5) becomes with this choice the well-known Hartree–Fock equation. The virtual orbitals are calculated in the field of the nucleus and all N electrons and usually lie in the continuum. Later, Kelly showed[10] that the alternative choice

$$V^{N-1}=\sum_{i=1}^{N-1} (J_i-K_i) \tag{7}$$

yields both bound and unbound virtual orbitals and greatly enhances the convergence of the perturbation series for the $2s^2$ pair correlation in Be. The occupied orbitals obtained using this potential are not all identical with Hartree–Fock ones, and additional perturbation corrections must therefore be considered. The potential proposed by Silverstone and Yin[11] and by Huzinaga and Arnau[12] and used for MBPT calculations by Miller and Kelly[13] combines the advantages of V^N and V^{N-1}. This Silverstone–Huzinaga potential[14] is defined as

$$V_{\text{SH}}=V^N+(1-P)\Omega(1-P) , \tag{8}$$

where P is the projection operator

$$P=\sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \tag{9}$$

and

$$\Omega=V^{N-1}-V^N . \tag{10}$$

It is easily verified that the occupied orbitals are Hartree–Fock orbitals, since

$$V_{\text{SH}}\varphi_k=V^N\varphi_k , \quad k\leq N \tag{11}$$

whereas virtual orbitals satisfy

$$V_{\text{SH}}\varphi_k=(V^{N-1}-P\Omega)\varphi_k , \qquad k>N \tag{12}$$

with $P\Omega$ modifying V^{N-1} only slightly.[13] In addition to V^N, two varieties of V_{SH} are made use of in the present work: The potential obtained when a $1s$ electron is left out of the summation in Eq. (7) is denoted V_{SH}^1, and leaving a $2s$ electron out gives V_{SH}^2. The zero-order Hamiltonian constructed with one of these potentials [Eq. (2)] is diagonalized within the basis sets described below to yield the hole and particle states for the MBPT calculations.

B. Basis Oribtals

A finite analytical basis set is, of necessity, incomplete, and care must be taken to assure proper spanning of the function space. This problem appears in all calculations performed by the expansion method, and the considerable experience accumulated may be of help in work of the kind presented here. Schulman and Kaufman's basis set[9] consists of Gaussian orbitals with a wide range of exponents, covering different regions in coordinate space. An alternative method used by Nesbet[15] is to employ Slater orbitals with different nl values having the same exponent (the set of all such orbitals forms a basis to the space of square-integrable functions). A possible guide for choosing the exponent is the overlap with occupied orbitals.[16] A related question, not answered in the present paper which reports calculations of Be correlation energy only, is the dependence of the basis set on the property to be calculated. Schulman and Kaufman[9] used the same set for calculating different properties of the hydrogen molecule with encouraging results, but further research into this point is needed.

The basis sets we used to expand Be orbitals consisted of Slater functions. Clementi's double-zeta set[17] ($1s$ with exponents 3.3370 and 5.5063, $2s$ with exponents 0.6040 and 1.0118) was augmented by s, p, d, and f orbitals with exponents taken from Nesbet.[15] Different exponents were used for $1s$ and $2s$ intrashell correlation, since the occupied orbitals are concentrated in different

TABLE I. Second-order $2s^2$ correlation-energy diagrams as function of basis-set size (a.u.). V^2_{SH} potential. Diagonal higher-order terms included by shifted denominators [Eq. (16)].

ns[a]	$E_2(s)$	np[a]	$E_2(p)$	nd[a]	$E_2(d)$	nf[a]	$E_2(f)$
7	−0.003 209	5	−0.050 010	4	−0.005 095	3	−0.001 314
8	−0.003 164	7	−0.049 868	5	−0.005 077	4	−0.001 349
9	−0.003 144	10	−0.049 798	7	−0.005 049		

[a] Number of basis orbitals with the relevant l values in the set. Basis sets are similar to the $2s^2$ set described in the text. The p, d, and f terms are calculated with a basis set including 9 s orbitals, to assure consistent expansion of the hole states.

regions in space. Basis orbitals were added until satisfactory convergence [better than 10^{-4} a.u.,[18] $(2-5)\times 10^{-5}$ a.u. in most cases] of second-order perturbation terms was achieved. A typical example is shown in Table I for $2s$ intrashell second-order diagrams with diagonal contributions of higher-order diagrams included as described in Sec. IV. Convergence for the $1s$ set was slightly faster.

The basis sets used to obtain the results reported below were as follows: For $1s^2$ correlation, the Slater orbitals $2s$-$6s$, $2p$-$8p$, $3d$-$7d$, and $4f$-$7f$ with the exponent 7.814 were added to Clementi's orbitals to form a $9s\,7p\,5d\,4f$ set; a similar set was used for $2s^2$ correlation, except that the exponent was 1.419 and the additional s orbitals had principal quantum numbers from 3 to 7, inclusive. Both exponents had to be included for $1s$-$2s$ intershell correlation, and we employed a $10s\,8p\,6d\,4f$ set consisting of Clementi's orbitals, $2s$-$4s$ orbitals with the exponent 7.814, $3s$-$5s$ with 1.419, and $2p$-$5p$, $3d$-$5d$, and $4f$-$5f$ orbitals with both exponents. Nesbet's atomic programs,[19] modified slightly to allow the application of the V_{SH} potential, were used to solve the Hartree-Fock equations and obtain integrals over Hartree-Fock orbitals for diagram evaluation. The orbital energy spectrum of the basis sets described above is given in Table II. In addition, the third column of the table shows eigenvalues obtained with a $2s$ set of a different size. Comparison with Table I indicates that convergence of energy diagrams is achieved in spite of the considerable change in the one-electron spectrum.

III. COMPARISON OF NUMERICAL AND ANALYTICAL CALCULATIONS

Second-order and third-order diagrams contributing to pair correlation in the Be atom appear in Fig. 1. Diagrams differing from those present by electron exchange along one or more interaction lines or by reflection in a vertical plane have been suppressed. Fig. 1(a) is the second-order diagram

$$E_2=\sum_{k_1k_2}\frac{|\langle pq|v|k_1k_2\rangle|^2}{D}\ , \tag{13}$$

where

$$D=\epsilon_p+\epsilon_q-\epsilon_{k_1}-\epsilon_{k_2}\quad . \tag{14}$$

TABLE II. Orbital energies, in a.u., of different basis sets described in Sec. II B. V^2_{SH} potential.

$1s$ set $9s\,7p\,5d\,4f$	$2s$ set $9s\,7p\,5d\,4f$	$2s$ set[a] $(8s)10p\,7d$	$1s$–$2s$ set $10s\,8p\,6d\,4f$
	s orbitals		
−4.732 69	−4.732 59	−4.732 53	−4.732 64
−0.309 24	−0.309 27	−0.309 26	−0.309 26
−0.061 44	−0.090 89	−0.088 98	−0.086 01
1.181 18	0.016 08	0.052 14	0.107 15
6.052 66	0.258 10	0.421 09	0.669 02
17.421 8	0.800 80	1.383 29	2.351 52
44.029 3	2.143 07	4.842 70	7.379 66
122.337	6.821 84	30.171 2	21.715 0
561.266	38.045 5		67.224 2
			328.588
	p orbitals		
0.565 51	−0.179 39	−0.179 41	−0.177 39
4.218 04	−0.044 62	−0.064 08	0.045 59
11.562 2	0.130 47	0.019 10	0.553 91
25.606 6	0.484 88	0.163 65	1.940 84
54.673 1	1.209 35	0.403 95	6.381 09
128.050	3.045 43	0.804 61	18.714 1
421.329	9.943 81	1.520 18	52.931 3
		2.934 75	192.878
		6.467 43	
		19.999 8	
	d orbitals		
3.117 80	−0.022 68	−0.043 91	0.037 91
10.734 8	0.177 11	0.066 74	0.487 34
26.721 6	0.610 76	0.276 81	1.861 09
64.364 0	1.634 80	0.661 13	8.705 69
189.712	4.988 48	1.406 84	28.845 5
		3.113 22	98.862 4
		8.660 94	
	f orbitals		
5.899 46	0.077 24		0.265 96
17.425 9	0.403 53		1.324 64
43.315 7	1.145 43		13.938 8
119.976	3.322 26		53.752 1

[a] The p and d orbital energies obtained with a $9s\,10p\,7d$ set.

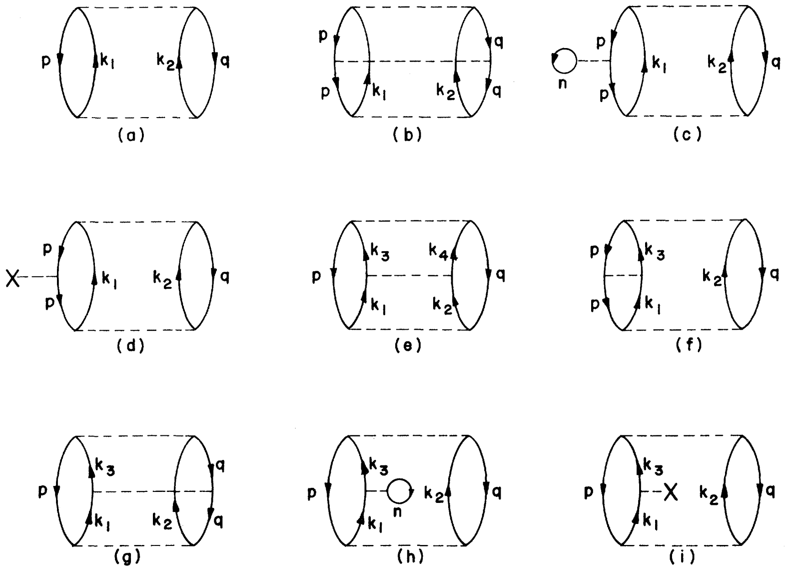

FIG. 1. Second- and third-order energy diagrams. Diagrams obtainable by electron exchange or by interchanging p and q are omitted. Cross represents interaction with the one-electron potential V.

Exchange terms are assumed to be included in Eq. (13) and throughout this paper. The hole-potential diagram 1(d) cancels 1(c) for all choices of V considered here, and the remaining hole-hole interaction 1(b) may be included to all orders in the second-order term of Eq. (13) by a denominator shift[3]

$$D' = D - \langle pq | v | pq \rangle \ . \tag{15}$$

Diagrams 1(h) and 1(i) cancel mutually when V^N of Eq. (6) is used as the one-electron potential. The

TABLE III. Second-order and third-order correlation terms of beryllium. V^N potential. Unless noted otherwise, all terms include higher-order hole-hole interactions by the denominator shift of Eq. (15). Energies are in a.u. (Be).

		$1s^2$ terms		$2s^2$ terms	
		Present work	Kelly[a]	Present work	Kelly[a]
Second order, unshifted	s	−0.012 48		−0.002 40	−0.002 41
	p	−0.022 49	−0.022 55	−0.022 20	−0.022 28
	d	−0.003 50		−0.003 78	−0.003 83
Second order	s	−0.011 49	−0.011 52	−0.001 92	−0.001 92
	p	−0.020 72	−0.020 77	−0.016 03	−0.016 05
	d	−0.003 35	−0.003 45	−0.003 20	−0.003 26
	f	−0.000 90		−0.001 00	
Third order Fig. 1(f)	s	−0.000 815	(−0.000 884)	−0.000 324	(−0.000 352)
	p	−0.001 417	(−0.001 581)	−0.004 512	−0.004 569
	d	−0.000 111		−0.000 467	(−0.000 527)
Exchange of Fig. 1(f)	s	0.000 207	(0.000 210)	0.000 055	(0.000 053)
	p	0.000 274	(0.000 270)	0.000 983	0.000 987
	d	0.000 008		0.000 046	(0.000 046)
Fig. 1(e)	s	0.000 902	(0.001 012)	0.000 354	(0.000 317)
	p	0.001 816	(0.002 120)	0.006 124	(0.005 803)
	d	0.000 163		0.000 709	(0.000 676)
$1s$-$2s$		Fig. 1(a)[b]		Exchange of Fig. 1(a)[c]	
Second order	s	−0.002 040	−0.002 033	0.000 994	0.000 990
	p	−0.004 736	−0.004 719	0.001 106	0.001 108
	d	−0.000 568	−0.000 612	0.000 194	(0.000 30)
	f	−0.000 085		0.000 035	

[a] Reference 3. Terms calculated approximately are shown in parentheses.

[b] Summed over the four $1s$-$2s$ pairs.

[c] Summed over $1s\alpha\, 2s\alpha$ and $1s\beta\, 2s\beta$ pairs.

only third-order energies to be calculated in this case are therefore represented by the ladder diagram 1(e) and the hole-particle interactions 1(f) and 1(g). Table III lists second-order and third-order contributions to $1s^2$ and $2s^2$ pair-correlation energies in Be, as well as second-order $1s$-$2s$ terms. These values were obtained using the V^N potential and including higher-order hole-hole interaction by shifting the denominator [Eq. (15)]. Kelly's corresponding numbers calculated with numerical orbitals[3] are included for comparison. The largest deviation from diagrams evaluated *exactly* by Kelly is 10^{-4} a.u., and the average difference is 3×10^{-5} a.u., which is quite satisfactory, coinciding with the convergence of the diagrams. Larger disagreement appears in Table III for terms calculated by Kelly with the help of the geometric approximation,[3] particularly for the ladder diagram [Fig. 1(e)], but we believe that these differences reflect the inaccuracies of Kelly's approximate results and not expansion errors.

IV. CORRELATION ENERGY OF THE BERYLLIUM ATOM

A. Denominator Shifts

We proceed now to calculate the correlation energy of the beryllium atom. Kelly has shown[3,4,13] that hole-hole and hole-potential interactions [Fig. 1(b)–1(d)], together with diagonal contributions to third- and higher-order corrections [Fig. 1(e)–1(i) with $k_1 = k_3$ and $k_2 = k_4$] and terms he called "rearrangement diagrams," may be included in the second-order diagram by substituting the shifted denominator[13]

$$D'' = D + \Delta + \Delta_{\text{corr}} \tag{16}$$

in Eq. (13), where

$$\Delta = -\langle pq|v|pq\rangle - \langle k_1k_2|v|k_1k_2\rangle + \langle pk_2|v|pk_2\rangle + \langle qk_1|v|qk_1\rangle - \Big(\sum_{n\neq p}\langle nk_1|v|nk_1\rangle - \langle k_1|V|k_1\rangle\Big) - \Big(\sum_{n\neq q}\langle nk_2|v|nk_2\rangle - \langle k_2|V|k_2\rangle\Big) + \Big(\sum_{n}\langle np|v|np\rangle - \langle p|V|p\rangle\Big) + \Big(\sum_{n}\langle nq|v|nq\rangle - \langle q|V|q\rangle\Big) \tag{17}$$

with exchange terms included, and

$$\Delta_{\text{corr}} = E_{\text{corr}}(p,q) + \sum_{r\neq q} E_{\text{corr}}(p,r) + \sum_{r\neq p} E_{\text{corr}}(r,q) + E'_{\text{corr}}(k_1,k_2)\ . \tag{18}$$

$E_{\text{corr}}(p,q)$ is the correlation energy of the pq pair, and $E_{\text{corr}}(p,r)$ and $E_{\text{corr}}(r,q)$ have a similar meaning. $E'_{\text{corr}}(k_1,k_2)$, the sum of diagrams with particle lines k_1 and k_2 and hole lines other than p and q, is rather awkward to include in our formulation, since not all pair correlations are calculated with the same particle states. This term is small relative to the total denominator, and we therefore neglected it. The other terms of Eq. (18) make it necessary to calculate correlation iteratively, since they appear in expressions for individual diagrams and are in turn modified by these diagrams. This does not present a serious problem, as Δ_{corr} is only a small shift. All the results quoted in this section were calculated with the shifted denominator of Eq. (16).

B. $2s^2$ Correlation

The advantage of using V^2_{SH} or V^{N-1} in the expression for the zero-order Hamiltonian [Eq. (2)] is that diagrams 1(f), 1(h), and 1(i) cancel out when p and q are $2s$ states. The third-order effects $E_3(l)$ not included in the second-order terms $E_2(l)$ by denominator shifts consist of the nondiagonal diagrams 1(e) and 1(g), with the latter counted twice to allow for the two possible interactions between hole and particle lines. Only diagrams with all particle lines having the same l value are considered here. $E_2(l)$ and $E_3(l)$ calculated with the V^2_{SH} potential for $0\leq l\leq 3$ are presented in Table IV. Following Kelly,[3,4] we define enhancement coefficients

$$C_l = E_3(l)/E_2(l) \tag{19}$$

and approximate nondiagonal higher-order effects by assuming they form a geometric progression. This progression is then summed to

$$E(l) = E_2(l)/(1 - C_l)\ . \tag{20}$$

Unlike Kelly, who applied the geometric approximation to most third-order terms,[3,4] we use it for fourth- and higher-order corrections only. These corrections are rather small, and our $E(l)$ values should therefore be more accurate than Kelly's.

Other contributions to $2s^2$ correlation come from ladders [Fig. 1(e)] where the intermediate interaction changes the l of the particle lines. These $E_3(l,l')$ terms are corrected for higher-order effects by

$$E(l,l') = E_3(l,l')/[(1 - C_l)(1 - C_{l'})]\ . \tag{21}$$

Ladders with two l changes may be approximated by

$$E(l,l',l'') = E(l,l')\,C_{l'l''}\ , \tag{22}$$

where

TABLE IV. $1s^2$ and $2s^2$ correlation energy (a.u.). V_{SH}^2 potential. Denominators shifted as in Eq. (16).

		$1s^2$		$2s^2$	
		Present work	Kelly[a]	Present work	Kelly[a]
$E_2(l)$	s	−0.013144		−0.003144	
	p	−0.023786		−0.049868	
	d	−0.003631		−0.005077	
	f	−0.000945		−0.001349	
	sum	−0.041506		−0.059349	
$E_3(l)$	s	−0.000686		−0.000194	
	p	−0.000904		0.007963	
	d	−0.000012		0.000391	
	f	0.000004		0.000090	
	sum	−0.001599		0.008250	
$E(l)$	s	−0.013869	−0.01408	−0.003352	−0.003704
	p	−0.024726	−0.02518	−0.043002	−0.04357
	d	−0.003642	−0.00414	−0.004714	−0.005321
	f	−0.000942		−0.001265	
	sum	−0.043179		−0.052332	
$E(l,l')$	sp	0.000278	0.000412	0.000954	0.00203
	sd	0.000050		0.000132	
	pd	0.000296	0.000226	0.003277	0.00282
	sf	0.000013		0.000040	
	pf	0.000075		0.000809	
	df	0.000034		0.000267	
	sum[b]	0.001492		0.010957	
$E(l,l',l'')$		−0.000081		−0.004819	
Three and four l changes				0.000810	
Total		−0.041767	−0.04212	−0.045374	−0.04488

[a] References 3 and 10. Most third-order terms approximated.

[b] Including terms with $l > l'$.

$$C_{l'l''} = E(l', l'')/E(l') \ . \qquad (23)$$

The sum of these terms is −0.004819 a.u., with the largest contribution coming from $E(p, d, p) = -0.002278$ and $E(p, f, p) = -0.000517$ a.u. $E(p, d, p)$ was also calculated directly to check the validity of Eq. (22); agreement was within 5×10^{-5} a.u. The same approximation was used to evaluate ladders with three and four l changes; they gave 0.001301 and −0.000491 a.u., respectively.

There are several sources of errors in the calculations reported above. The contribution of particle states with $l > 3$ is estimated to be $(-4\pm2)\times10^{-4}$ a.u. The expansion error due to incompleteness of basis sets is put at 3×10^{-4}, and the error of approximating high-order corrections should not be greater than 4×10^{-4} a.u. The correlation energy of the $2s^2$ pair of beryllium as calculated by us is therefore -0.0458 ± 0.0009 a.u. This should be compared with Kelly's corrected value[3,10] of −0.04488 a.u. and Nesbet's[15] −0.04535 a.u.

C. $1s^2$ Correlation

Contributions to the $1s^2$ intrashell correlation calculated with the V_{SH}^2 potential appear in Table IV. The third-order terms include the diagrams 1(e), 1(f) and its exchange, 1(g) [numerically equal to 1(f)], and 1(h) and its exchange with $2s$ on the hole line n. All these diagrams, except 1(e), are counted twice. Another calculation of the $1s^2$ energy was carried out with the V_{SH}^1 potential. Only 1(e) and 1(g) contribute in this case to the third-order diagrams, which turn out to be an order of magnitude lower than the value shown in Table IV. The total $1s^2$ correlation-energy values agree however within 10^{-5} a.u. Particle states with $l > 3$ are believed to contribute $(-3\pm1)\times10^{-4}$ a.u. The expansion error is put at 3×10^{-4} a.u., and the error of approximating high-order effects is negligible since these effects themselves are small. We obtain therefore a $1s^2$ correlation energy of -0.0421 ± 0.0004, compared with Kelly's[3] −0.04212 a.u. and Nesbet's[15] −0.04183 a.u.

D. 1s-2s Pair Correlation

The intershell 1s-2s pair correlation is an order of magnitude lower than $1s^2$ and $2s^2$ energies. Only the second-order terms of Fig. 1(a) and its exchange were therefore calculated, with some higher-order effects included by denominator shifts. Results obtained with the V^2_{SH} potential are presented in Table V. The $1s\alpha\, 2s\alpha$ energies are smaller than $1s\alpha\, 2s\beta$ ones because of partial cancellation of direct and exchange diagrams for the former. These values, multiplied by two to account for the $1s\beta 2s\alpha$ and $1s\beta 2s\beta$ pairs, give −0.00592 a.u. Estimating higher-order effects not included in Table V, we put the total 1s-2s pair correlation at −0.0054 ± 0.0004 a.u., compared to Kelly's[3] −0.00497 a.u. (only hole-hole interactions included in the denominator shift) and Nesbet's[15] −0.00586 a.u.

E. Three-Body Terms

Three-body contributions to the correlation energy are described by the ring diagram of Fig. 2 with p, q, and r all different, with all diagrams obtainable therefrom by exchange along one or more interaction lines included. Results for $1s^2 2s$ and $1s2s^2$ electron triples obtained with the V^2_{SH} potential and shifted denominators are collected in Table VI. Accounting for the four electron triples of Be and correcting for nondiagonal higher-order terms, we estimate the three-body energy at 0.0011 ± 0.0002 a.u., compared with Kelly's[3] 0.0005 a.u. and Nesbet's[15] 0.0009 a.u.

F. Total Correlation Energy

The separate contributions of electron pairs and triples to the correlation energy of Be are summed in Table VII. The total of −0.0922 ± 0.0019 a.u. is in good agreement with the "experimental"[15] −0.0939 a.u. Kelly's corrected value,[3,10] obtained by numerical MBPT calculations with s, p, and d orbitals only and approximating most third-order diagrams, is −0.092 ± 0.004 a.u. and Nesbet's Bethe-Goldstone calculations[15] give −0.0921 a.u.

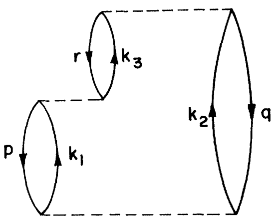

FIG. 2. Three-body diagram. p, q, and r represent different hole states. There are seven other diagrams [e.g., Fig. 1(f) and 1(g) with hole states all different] obtainable by electron exchange along one or more interaction lines of the pictured ring diagram.

V. CONCLUSIONS

The purpose of this paper is to investigate the feasibility of carrying our MBPT correlation-energy calculations by expanding the particle and hole orbitals in a finite set of bound-type functions. Three tests are applied, with the Be atom serving as a test case: convergence of individual diagrams with respect to basis set size, their agreement with values obtained by the numerical method, and agreement of the total correlation energy with experiment. The first two tests are satisfied within 10^{-4} a.u. by $9s\, 7p\, 5d\, 4f$ Slater-type orbital sets for intrashell correlation and a $10s\, 8p\, 6d\, 4f$ set for the intershell effects. The same sets satisfy the third criterion, too. These results indicate that MBPT calculations by the expansion method are indeed feasible. A point that remains to be investigated is the dependence of the basis orbitals on the property to be calculated.

The use of finite, bound-type basis sets for MBPT calculations has several advantages over the more common numerical method, such as the uniform handling of particle states with negative and positive energies and the elimination of cumbersome integrations over continuum states. The most serious disadvantage of the expansion method is the need to search for satisfactory basis sets. The considerable experience gained in variational calculations with finite basis sets should provide useful hints (see Sec. II B), and our results indicate that such criteria as the spatial distribution of excited orbitals and their overlap with occupied orbitals may be applicable here as they are in variational work.[16] Thus, the set used to describe the 2s correlation is much more diffuse than the 1s set. In general, it cannot be expected that a single basis set of reasonable size will be adequate to describe the different correlation effects. (A related

TABLE V. 1s-2s pair correlation (a.u.). V^2_{SH} potential. Denominators as in Eq. (16).

		$1s\alpha\, 2s\alpha$	$1s\alpha\, 2s\beta$
$E_2(l)$	s	−0.000015	−0.000571
	p	−0.000753	−0.001385
	d	−0.000051	−0.000158
	f	−0.000004	−0.000023
	sum	−0.000823	−0.002137

TABLE VI. Three-body correlations (a.u.). V^2_{SH} potential. Shifted denominators. The ring diagram (Fig. 2) and all its exchanges are included.

	$1s^2 2s$	$1s\, 2s^2$
s	−0.000019	−0.000006
p	0.000083	0.000593
$d+f$	10^{-7}	0.000005
sum	0.000062	0.000592

TABLE VII. Correlation energy of Be (a.u.).

$1s^2$	-0.0421 ± 0.0004
$2s^2$	-0.0458 ± 0.0009
$1s$-$2s$	-0.0054 ± 0.0004
Total pair correlation	-0.0933 ± 0.0017
Three-body	0.0011 ± 0.0002
Total	-0.0922 ± 0.0019

phenomenon is encountered in Kelly's Be calculations, where different continuum orbitals are used to calculate 1*s* and 2*s* correlation.[3]) Each electron shell will probably require a different basis set, with intershell effects (usually smaller than intrashell ones) calculated in a mixed set, comprising the most important orbitals of the relevant intrashell sets.

The necessary search for adequate basis sets will probably make the application of the expansion method to *atomic* systems less convenient than the conventional numeric MBPT. The potential of the method lies in the realm of *molecular* calculations. An acceptable zero-order Hamiltonian must have easily obtainable eigenfunctions, while not leaving off too large a perturbation. No such Hamiltonian suitable for numerical MBPT calculations on a variety of molecules has been proposed. The use of a one-center operator has adverse effects on the convergence of the perturbation series even for the H_2O molecule,[6(c)] and a similar approach to molecules with several atoms heavier than hydrogen is hopeless. The application of the expansion MBPT method to molecules, on the other hand, is not very much different from the atomic application presented above (except for such problems as the calculation of many-center integrals), and investigations in this direction are now in progress.

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