

## MØLLER-PLESSET CALCULATIONS TAKING CARE OF THE CORRELATION CUSP

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Received 3 November 1986; in final form 28 November 1986

Møller-Plesset calculations to second order have been carried out on the ten-electron systems Ne, HF and H<sub>2</sub>O with a new functional, including  $r_{12}$ -dependent pair correlation functions, which takes care of the correlation cusp. The calculated second-order pair energies are accurate to within a few millihartree in comparison with the estimated exact values. In particular, second-order energies of 384.2, 380.1 and 362.9 mE<sub>h</sub> have been obtained for Ne, HF and H<sub>2</sub>O respectively.

### 1. Introduction

It has been known for a long time that accurate electronic structure calculations of atoms or molecules are only possible if the correlation cusp is correctly accounted for. There is a vast literature on variational calculations with wavefunctions that contain  $r_{ij}$ -dependent terms of various complexity, with linear (e.g. ref. [1]) or non-linear (e.g. ref. [2]) variational parameters (the most important references are quoted in ref. [3]). We have shown [3] that for the simplest two-electron system, the He atom, the non-relativistic (clamped nucleus) ground-state energy can be obtained very accurately with the ansatz

$$\psi(1,2) = \frac{1}{2} r_{12} \phi(1,2) + \chi(1,2), \quad (1)$$

where  $\phi$  is the eigenfunction of the He atom *without* electron interaction, and  $\chi$  is expanded in products of one-electron functions  $\phi_p(1) \phi_q(2)$  (in conventional CI the entire  $\psi$  is expanded in such products). Limiting the angular quantum number  $l$  of the basis functions to  $l=0$  and  $l=1$  we get  $E_0(\text{He})$  accurate to  $\approx 0.1$  mE<sub>h</sub>; with  $l$  up to 5 accurate to 1  $\mu$ E<sub>h</sub>. To achieve the same accuracy in conventional CI  $l$  up to 6 or up to 50, respectively, is required [4].

A similarly rapid convergence is obtained with the ansatz (1) for the energy in second-order perturbation theory (in the  $1/Z$  expansion). In this case we could show [3] that the partial wave contributions  $\tilde{E}_l$  due to  $\chi_l$  go as  $(l+1/2)^{-8}$  as contrasted with conventional partial wave contributions  $E_l$  that go as  $(l+1/2)^{-4}$ .

It is straightforward to take advantage of these results for larger electronic systems. For systems with more than two electrons two independent convergence problems arise: (a) the convergence with the size of the one-electron basis; (b) the convergence with the "excitation" rank (single, double, triple, etc., "excitations") in a CI or a coupled-cluster (CC) calculation or the convergence with the order in perturbation theory.

Since we are concerned in this work with convergence problem (a) we have considered only a single level of problem (b). The simplest non-trivial level in this sense is Møller-Plesset perturbation theory to second order [5]. On this level many reference calculations with conventional expansions and also some extrapolations to complete basis sets are available for comparison.

### 2. Method

We start from the Hylleraas functional for the second-order energy (with  $\phi$  the zeroth- and  $\psi$  the first-order wavefunction)

$$F(\psi) = 2 \operatorname{Re} \langle \psi | V - E_1 | \phi \rangle + \langle \psi | H_0 - E_0 | \psi \rangle \geq E^{(2)}. \quad (2)$$

If  $\phi$  is the (restricted) Hartree-Fock function,  $F(\psi)$  decouples into a sum of pair contributions

$$F(\psi) = \sum_{i < j} f(u_{ij}), \quad (3)$$

$$f(u_{ij}) = 2 \operatorname{Re} \langle [ij] | r_{12}^{-1} | u_{ij}(1,2) \rangle + \langle u_{ij}(1,2) | F(1) + F(2) - \epsilon_i - \epsilon_j | u_{ij}(1,2) \rangle, \quad (4)$$

$$[pq] = 2^{-1/2} [\varphi_p(1) \varphi_q(2) - \varphi_q(1) \varphi_p(2)]. \quad (5)$$

The  $u_{ij}(1,2)$  are, by virtue of the Brillouin theorem, strongly orthogonal to all the occupied  $\varphi$ .

We make the ansatz

$$u_{ij}(1,2) = \frac{1}{2} c_{ij} \{1 - P(1)\} \{1 - P(2)\} r_{12} [ij] + w_{ij}(1,2), \quad (6)$$

$$P(1) = \sum_k |\varphi_k(1)\rangle \langle \varphi_k(1)|, \quad (7)$$

$$w_{ij}(1,2) = \sum_{a < b} d_{ij}^{ab} [ab], \quad (8)$$

where labels  $i, j, k, \dots$  always refer to spin orbitals occupied in  $\phi$ ,  $a, b, c, \dots$ , to unoccupied and  $p, q, r, \dots$  to arbitrary spin orbitals. The  $c_{ij}$  and  $d_{ij}^{ab}$  are linear variational parameters.

In order to evaluate (4) with the ansatz (6), we make a few assumptions and approximations:

(a) We assume that the  $\varphi$  are eigenfunctions of the exact Fock operator rather than of its approximation in the finite basis  $\{\varphi\}$ . This allows the reformulation

$$\begin{aligned} \langle F(1) + F(2) - \epsilon_i - \epsilon_j \rangle \frac{1}{2} r_{12} [ij] &= \frac{1}{2} [F(1) + F(2), r_{12}] [ij] \\ &= \frac{1}{2} [T(1) + T(2), r_{12}] [ij] - \frac{1}{2} [K(1) + K(2), r_{12}] [ij] \\ &= (r_{12}/r_{12}) (\nabla_1 - \nabla_2) [ij] - r_{12}^{-1} [ij] - \frac{1}{2} [K(1) + K(2), r_{12}] [ij], \end{aligned} \quad (9)$$

where  $T$  is the kinetic energy operator and  $K$  the exchange operator. The Coulomb operator is local and commutes with  $r_{12}$ .

(b) We approximate the commutator of  $K$  and  $r_{12}$  by means of a completeness insertion, i.e. via matrix products. We do the same with the double commutator  $[[K, r_{12}], r_{12}]$ .

(c) Terms with one projector are evaluated by means of the completeness insertion

$$\langle [ij] | r_{12} P^{(1)} r_{12}^{-1} | [ij] \rangle = \sum_{k,p} \langle [ij] | r_{12} | \varphi_k(1) \varphi_p(2) \rangle \langle \varphi_k(1) \varphi_p(2) | r_{12}^{-1} | [ij] \rangle. \quad (10)$$

Common to all three assumptions or approximations is the fact that they become exact in the limit of a complete basis, i.e. the corresponding errors vanish with increasing basis size. It is important that these errors vanish much faster with the angular quantum number  $l$ , than do the basis unsaturation errors in a conventional calculation without the  $r_{12}$  term. The latter definitely go as  $(l+1/2)^{-4}$ , while the errors due to our three assumptions appear to decrease faster than  $(l+1/2)^{-6}$ . For atoms, completeness of the basis for a finite number of  $l$  values is sufficient to make the errors due to assumptions (a) and (c) vanish.

As is the case for the He ground state the  $(l+1/2)^{-4}$  dependence of conventional partial wave contributions to any of the second-order pair energies is due to the attempt to evaluate the expressions

$$\langle [ij] | r_{12} r_{12}^{-1} | [ij] \rangle = 1, \quad (11)$$

$$\langle [ij] | r_{12} (r_{12}/r_{12}) (\nabla_1 - \nabla_2) | [ij] \rangle = \frac{3}{2} \quad (12)$$

(that we evaluate exactly) by means of the expansions

$$\sum_{p < q} \langle [ij] | r_{12} | [pq] \rangle \langle [pq] | r_{12}^{-1} | [ij] \rangle, \quad (13)$$

$$\sum_{p < q} \langle [ij] | r_{12} | [pq] \rangle \langle [pq] | (r_{12}/r_{12})(\nabla_1 - \nabla_2) | [ij] \rangle, \quad (14)$$

or rather through their counterparts for singlet and triplet pairs. For singlet pairs the error in (13) vanishes as  $(l+1/2)^{-4}$ , that of (14) as  $(l+1/2)^{-6}$ , for triplet pairs both go as  $(l+1/2)^{-6}$  and approach the ratio  $-1$  for  $l \rightarrow \infty$ .

It should be noted that approximation (10) is not necessary. The corresponding integral could be evaluated exactly as

$$\langle [ij] | r_{12}^{-1} P(1) r_{12} | [ij] \rangle = \sum_k \int [ij(1,2)] r_{12}^{-1} \phi_k(1) \phi_k(3) r_{32} [ij(3,2)] d\tau_1 d\tau_2 d\tau_3. \quad (15)$$

This requires a one-dimensional numerical integration. All other integrals needed in our calculations are evaluated in closed form. The formulae are relatively simple if one uses Gaussian lobes rather than Cartesian Gaussians [6]. We have taken advantage of this.

The final expressions for the second-order pair energies are

$$f_{ij} = e_{ij} + (2c_{ij} - c_{ij}^2) V_{ij} + c_{ij}^2 U_{ij}, \quad (16)$$

where  $e_{ij}$  is the conventional second-order pair energy in the same basis and

$$V_{ij} = \frac{1}{2} - \frac{1}{2} \sum_{p < q} \langle [ij] | r_{12} | [pq] \rangle \langle [pq] | r_{12}^{-1} | [ij] \rangle, \quad (17)$$

$$U_{ij} = \frac{3}{4} - \frac{1}{2} \sum_{p < q} \langle [ij] | r_{12} | [pq] \rangle \langle [pq] | (r_{12}/r_{12})(\nabla_1 - \nabla_2) | [ij] \rangle. \quad (18)$$

The  $V_{ij}$  and  $U_{ij}$  vanish in the limit of a complete basis, they represent a ‘‘cusp correction’’ or ‘‘basis unsaturation correction’’. The  $f_{ij}$  are stationary with respect to variations of the  $c_{ij}$  if

$$c_{ij} = V_{ij} / (V_{ij} - U_{ij}) \quad (19)$$

then

$$f_{ij} = e_{ij} + c_{ij} V_{ij}. \quad (20)$$

For practical calculations we use a formalism in terms of singlet and triplet pairs rather than of pairs of spin orbitals.

### 3. Results

In table 1 the results of our calculations on the Ne atom are displayed. With a 12s8p4d1f basis a conventional MP2 calculation yields 87% of the estimated exact MP2 energy, with our ansatz and the same basis we recover 99% of the supposedly exact value [7]; the best calculated value of Jankowski et al. [7] with  $l$  up to 10 is 99.5% of the estimated exact value, while Lindgren and Salomonson [10] with  $l$  up to 6 obtain some 88.5% of the result extrapolated for  $l \rightarrow \infty$ .

For  $E^{(2)}$  for the Ne ground state two extrapolations to the exact values have been published [7,10]. We have used for comparison those of Jankowski et al. [7] because they are given separately for singlet and triplet pairs, and also because we regard their extrapolation as somewhat more reliable. The total extrapolated  $E^{(2)}$  values of the two references differ by  $\approx 1$  mE<sub>h</sub>. Our computed values could also be compared with those of Wenzel et

Table 1  
Second-order pair correlation energies for Ne <sup>a)</sup> in  $mE_h$

Pair <i>ij</i>		$-e_{ij}$	$-f_{ij}$	$-e_{ij}(JM)$	$c_{ij}$ <sup>b)</sup>
1s <sup>2</sup>	( <sup>1</sup> S)	36.05	40.02	40.22	0.87
1s2s	( <sup>1</sup> S)	3.52	3.88	3.97	0.69
	( <sup>3</sup> S)	1.47	1.56	1.59	0.29
2s <sup>2</sup>	( <sup>1</sup> S)	10.29	11.90	12.02	0.92
1s2p	( <sup>1</sup> P)	6.24	7.56	8.13	0.52
	( <sup>3</sup> P)	13.15	13.53	14.04	0.21
2s2p	( <sup>1</sup> P)	46.64	59.65	60.33	0.83
	( <sup>3</sup> P)	24.88	26.31	26.82	0.33
2p <sup>2</sup>	( <sup>1</sup> S+ <sup>1</sup> D)	112.63	133.97	133.41	0.75/0.83
	( <sup>3</sup> P)	83.66	85.85	87.39	0.28
total		338.52	384.24	387.92	

<sup>a)</sup> Conventional pair energies  $e_{ij}$  and pair energies  $f_{ij}$  (calculated by the new method in the same basis) are compared with the extrapolated results  $e_{ij}(JM)$  of Jankowski and Malinowski, ref. [7]. Details of basis set: 11s[5111111]7p Huzinaga basis set [8]+1s(0.12)+1p(0.86)+4d(0.575×4<sup>n-1</sup>; n=1,...,4)+1f(3.2). SCF energy: -128.544551  $E_h$ , best reference value -128.5471  $E_h$  [9].

<sup>b)</sup> Variational parameter (see text).

Table 2  
Second-order pair correlation energies for HF <sup>a)</sup> ( $R_{HF}=1.7328$  au) in  $mE_h$

Pair <i>ij</i>		$-e_{ij}$	$-f_{ij}$	$c_{ij}$
1σ <sup>2</sup>	( <sup>1</sup> Σ <sup>+</sup> )	31.29	40.56	0.70
1σ2σ	( <sup>1</sup> Σ <sup>+</sup> )	2.69	3.28	0.39
	( <sup>3</sup> Σ <sup>+</sup> )	1.30	1.46	0.14
2σ <sup>2</sup>	( <sup>1</sup> Σ <sup>+</sup> )	10.79	12.94	0.87
1σ3σ	( <sup>1</sup> Σ <sup>+</sup> )	0.46	1.90	0.34
	( <sup>3</sup> Σ <sup>+</sup> )	2.02	3.19	0.20
2σ3σ	( <sup>1</sup> Σ <sup>+</sup> )	15.41	19.95	0.61
	( <sup>3</sup> Σ <sup>+</sup> )	8.06	9.08	0.21
3σ <sup>2</sup>	( <sup>1</sup> Σ <sup>+</sup> )	25.21	28.49	0.44
1σ1π	( <sup>1</sup> Π)	0.73	4.65	0.35
	( <sup>3</sup> Π)	5.11	8.40	0.20
2σ1π	( <sup>1</sup> Π)	29.03	39.85	0.59
	( <sup>3</sup> Π)	16.69	19.64	0.22
3σ1π	( <sup>1</sup> Π)	25.53	33.08	0.47
	( <sup>3</sup> Π)	51.01	55.24	0.21
1π <sup>2</sup>	( <sup>1</sup> Σ <sup>+</sup> + <sup>1</sup> Δ)	55.90	70.37	0.46/0.48
	( <sup>3</sup> Σ <sup>-</sup> )	25.34	28.06	0.22
total		306.59	380.13	

<sup>a)</sup> See table 1. Details of basis set: 11s[5111111]7p[211111] Huzinaga basis set + 3d(0.0875,0.35,1.4)+1f(2.1) for fluorine and 10s[511111] Huzinaga basis set [12]+3p(0.1625,0.65,2.6) for hydrogen. SCF energy: -100.067840  $E_h$ , best reference value -100.07046  $E_h$  [9].

al. [11] using a basis of Gaussian geminals. The individual pair energies differ by some tenths of a millihartree and the total  $E^{(2)}$  by about 1  $mE_h$ .

For HF (table 2) no extrapolated reference values are available. However, for H<sub>2</sub>O (as well as for Ne) Petersson and Braunstein [13] have published results from a rather tricky extrapolation procedure based on an analysis of the natural orbital expansion of the pair functions. These values (included in table 3) are astonishingly close to our computed ones.

Table 3

Second-order pair correlation energies for H<sub>2</sub>O<sup>a)</sup> ( $R_{\text{OH}} = 1.81035$  au,  $\alpha_{\text{HOH}} = 104.4^\circ$ ) in  $E_h$ 

Pair $ij$	$-e_{ij}$			$-f_{ij}$			$-e_{ij}(\text{PB})$	$c_{ij}$ s/t
	singlet	triplet	sum	singlet	triplet	sum		
1a <sub>1</sub> <sup>2</sup>	31.51	—	31.51	40.87	—	40.87	40.95	0.70
1a <sub>1</sub> 2a <sub>1</sub>	2.45	1.28	3.73	2.92	1.42	4.34	5.03	0.36/0.14
1a <sub>1</sub> 1b <sub>2</sub>	0.47	1.99	2.46	1.32	2.52	3.84	3.91	0.37/0.20
1a <sub>1</sub> 3a <sub>1</sub>	0.82	2.44	3.26	1.90	3.11	5.01	5.26	0.39/0.20
1a <sub>1</sub> 1b <sub>1</sub>	0.65	2.88	3.53	1.94	3.69	5.64	6.00	0.37/0.20
2a <sub>1</sub> <sup>2</sup>	11.50	—	11.50	13.26	—	13.26	12.70	0.84
1b <sub>2</sub> <sup>2</sup>	23.13	—	23.13	25.07	—	25.07	25.25	0.56
3a <sub>1</sub> <sup>2</sup>	22.55	—	22.55	24.97	—	24.97	25.27	0.53
1b <sub>1</sub> <sup>2</sup>	22.57	—	22.57	25.30	—	25.30	25.61	0.48
2a <sub>1</sub> 1b <sub>2</sub>	17.57	7.70	25.27	21.10	8.07	29.17	29.44	0.76/0.22
2a <sub>1</sub> 3a <sub>1</sub>	14.36	7.95	22.31	17.15	8.41	25.56	27.43	0.67/0.21
2a <sub>1</sub> 1b <sub>1</sub>	14.98	8.66	23.64	18.14	9.31	27.45	28.63	0.63/0.21
1b <sub>2</sub> 3a <sub>1</sub>	15.71	22.85	38.57	17.24	23.46	40.71	42.72	0.51/0.21
1b <sub>2</sub> 1b <sub>1</sub>	12.18	24.46	36.64	14.03	25.21	39.24	39.86	0.49/0.20
3a <sub>1</sub> 1b <sub>1</sub>	13.95	25.26	39.21	16.48	26.12	42.60	43.05	0.54/0.19
total			309.89			353.03	361.11	

<sup>a)</sup> See table 1. Calculated pair energies are compared with extrapolated results  $e_{ij}(\text{PB})$  of Petersson and Braunstein [13]. Details of used basis set: 11s[5111111]7p[211111] Huzinaga basis set+2d+1f for oxygen and 6s[3111] Huzinaga basis set+3p[21]+2d[2] for hydrogen (polarization functions as in ref. [14]). SCF energy:  $-76.065122 E_h$ , best reference value  $-76.06674 E_h$  [14].

The error in the second-order correlation energy from our calculations is obviously of the order of a few ( $\approx 2-3$ ) millihartree. However, the errors in our SCF energies are of the same order of magnitude. This indicates, that in order to reduce the overall error by a factor of 10 or more, the convergence of the expansion in a Gaussian basis is too slow and one should use an ansatz that takes care of the nuclear cusp as well as the correlation cusp.

The best available Hartree-Fock energies to date for Ne and HF were obtained nearly 20 years ago by McLean and Yoshimine [9] using STO basis sets.

The calculations were performed on the CYBER 205 of the Ruhr-Universität Bochum.

## References

- [1] E.A. Hylleraas, Z. Physik 54 (1929) 347; 65 (1930) 209;  
C.L. Pekeris, Phys. Rev. 112 (1958) 1649; 126 (1962) 1470;  
J.S. Sims and S. Hagstrom, Phys. Rev. A4 (1971) 908; A11 (1975) 418;  
D.C. Clary and N.C. Handy, Chem. Phys. Letters 51 (1977) 483.
- [2] J.V. Longstaff and K. Singer, Theoret. Chim. Acta 2 (1964) 265;  
K.C. Pan and H.F. King, J. Chem. Phys. 53 (1970) 4397;  
L. Adamowitz and A. Sadlej, J. Chem. Phys. 67 (1977) 4298; 69 (1978) 3992;  
K. Szalewicz, B. Jeziorski, H.J. Monkhorst and J.G. Zabolitzky, J. Chem. Phys. 78 (1983) 1420; 79 (1983) 5543; 81 (1984) 368.
- [3] W. Kutzelnigg, Theoret. Chim. Acta 68 (1985) 445.
- [4] D.P. Carroll, H.J. Silverstone and R.M. Metzger, J. Chem. Phys. 71 (1979) 4142.
- [5] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [6] A. Preiskorn and B. Zurawski, Intern. J. Quantum Chem. 27 (1985) 641.

- [7] K. Jankowski and P. Malinowski, *Phys. Rev. A* 21 (1980) 45.
- [8] S. Huzinaga, *Approximate atomic functions*, University of Alberta, Edmonton (1971).
- [9] A.D. McLean and M. Yoshimine, *IBM J. Res. Dev.* (1967) supplement .
- [10] I. Lindgren and S. Salomonson, *Physica Scripta* 21 (1980) 335.
- [11] K. Wenzel, J.G. Zabolitzky, K. Szalewicz, B. Jeziorski and H.J. Monkhorst, to be published;  
H.J. Monkhorst, to be published;  
K. Wenzel and J.G. Zabolitzky, to be published.
- [12] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
- [13] G.A. Petersson and M. Braunstein, *J. Chem. Phys.* 83 (1985) 5129.
- [14] E.R. Davidson and D. Feller, *Chem. Phys. Letters* 104 (1984) 54