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# Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. III. Second-order Møller–Plesset (MP2-R12) calculations on molecules of first row atoms

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The MP2-R12 method (Møller–Plesset second-order perturbation theory with terms linear in the interelectronic coordinate  $r_{12}$ ) in the approximations A and B as outlined in paper I of this series is applied to the ground states of the molecules  $H_2$ , LiH, HF,  $H_2O$ ,  $NH_3$ ,  $CH_4$ ,  $Be_2$ ,  $N_2$ ,  $F_2$ ,  $C_2H_2$ , and CuH in their experimental equilibrium geometry, and to the van der Waals interaction between two He atoms. In all cases MP2 correlation energies are obtained that are supposed to differ by at most a few percent from the basis set limit. For  $CH_4$  the dependence of the energy on the symmetric stretching coordinate is studied, which together with other information leads to a recommended bond length of 1.086 Å for the CH bond length. For  $He_2$  and  $F_2$  the canonical and localized descriptions are compared. The latter is superior for the  $K$ -shell contributions, otherwise there is a little difference. For  $He_2$  in the localized representation rather good results for the dispersion interaction are obtained. The potential curve of  $Be_2$  is significantly improved in MP2-R12 as compared to conventional MP2. The examples  $C_2H_2$  and CuH show that the method is not limited to very small systems.

## I. INTRODUCTION

The MP2-R12 theory is now applied to molecules. A general outline of the theory has been given in paper I of this series<sup>1</sup> and a short description in part II<sup>2</sup> as well as in some previous papers.<sup>3–5</sup> The MP2-R12 method is mainly Møller–Plesset perturbation theory to second order with first order pair functions that contain terms linear in the interelectronic coordinates  $r_{ij}$ . Inclusion of these terms considerably speeds up the convergence of an expansion in a one-electron basis. In the atomic case the partial wave increments corresponding to basis functions of a given  $l$  go as  $(l + \frac{1}{2})^{-4}$  in a conventional calculation, but as  $(l + \frac{1}{2})^{-8}$  when the terms linear in  $r_{12}$  are included<sup>1,2</sup> using the approximation B described in paper I.<sup>1</sup>

In paper II of this series,<sup>2</sup> calculations on closed-shell atomic ground states from He to Kr were reported. There we have compared the results of calculations with a program written especially for atoms using STOs and angular momentum algebra, and of a general GTO program that can also be applied to molecules. With the “atomic program” we could afford to include basis functions with high  $l$  values and to make basis saturation tests, which would have been prohibitive with the molecular program. Nevertheless the latter turned out to be quite competitive. The total MP2-R12 correlation energies obtained with the molecular program differ generally by something of the order of 1% from the estimated basis limit results, while conventional MP2 calculations with the same basis sets reached between 70%–80% of the basis set limit MP2 energy. The MP2-R12 results were rather insensitive to details of the basis, provided that some fundamental requirements were satisfied, e.g., that for a calculation on Ne the basis contained up to  $f$  functions.

While theoretical considerations<sup>1</sup> as well as the experience with atomic calculations in terms of STOs<sup>2</sup> indicate that approximation B is superior to approximation A, in molecular calculations with GTOs, approximation A usually yields results closer to the estimated basis set limit than approximation B, although the difference between the MP2 energies for the two approximations is typically of the order of 1%.

A few comments on the “molecular MP2-R12 program” will be given in Sec. II. We shall then first discuss the very small molecules  $H_2$  and LiH, including the comparison with He and Be (Sec. III) and then report on calculations on the ten-electron systems HF,  $H_2O$ ,  $NH_3$ , and  $CH_4$  including Ne for comparison (Sec. IV). In the case of  $CH_4$  we shall try to settle an old controversy concerning its bond length. We then consider the diatomic nonhydride systems  $He_2$ ,  $Be_2$ ,  $N_2$ , and  $F_2$  (Sec. VI) where we compare an approach based on localized orbitals with that in terms of canonical orbitals. Although the differences are not very large, the localized approach is definitely superior. The potential curve of  $Be_2$  is much changed in going from MP2 to MP2-R12, i.e., from a finite basis to the limit of a complete basis. We finally consider some larger or heavier molecules like  $C_2H_2$  and CuH (Secs. VII and VIII). The study of  $C_2H_2$  has been challenged by the recent direct MP2 calculations of Saebø and Almlöf,<sup>6</sup> and CuH was a simple test case of a molecule involving a transition metal. An MP2-R12 study of the carbocations  $CH_5^+$ ,  $C_2H_3^+$ , and  $C_2H_5^+$  has been published elsewhere.<sup>5</sup>

## II. METHOD AND COMPUTER PROGRAM

The MP2-R12 method has been presented previously.<sup>1,3,4</sup> For a short description see Ref. 5. The MP2-R12 the-

ory in a localized representation is outlined in Appendix A. We give here a few comments on the evaluation of the integrals and the organization of the program.

We have used a basis of Gaussian lobe functions,<sup>7</sup>  $p$ ,  $d$ , etc. functions are constructed as linear contributions of Gaussian lobes.<sup>8</sup> When we made this choice, we still believed that we had to evaluate three- and four-electron integrals explicitly, which was not too difficult for Gaussian lobes,<sup>9</sup> but rather hard for cartesian Gaussians. Furthermore we had a lobe integral program available<sup>10</sup> that was quite efficiently vectorized for the CYBER 205. Again it is very hard, if not hopeless to write an efficiently vectorized code for the CYBER 205 in terms of cartesian Gaussians.

In the MP2-R12 method the following integrals are needed

- (a)  $\langle \varphi_p(1)\varphi_q(2) \left| \frac{1}{r_{12}} \right| \varphi_r(1)\varphi_s(2) \rangle$ ,  
 (b)  $\langle \varphi_p(1)\varphi_q(2) | r_{12} | \varphi_r(1)\varphi_s(2) \rangle$ ,  
 (c)  $\langle \varphi_p(1)\varphi_q(2) | r_{12}^2 | \varphi_r(1)\varphi_s(2) \rangle$ ,  
 (d)  $\langle \varphi_p(1)\varphi_q(2) \left| -\frac{1}{2} \frac{\mathbf{r}_{12}}{r_{12}} (\nabla_1 - \nabla_2) \right| \varphi_r(1)\varphi_s(2) \rangle$ .

The integrals of type (b) are by virtue of

$$r_{12} = (r_1^2 + r_2^2 - 2r_1r_2 \cos \vartheta_{12})^{1/2}$$

reduced to integrals of type (a), those of type (c) are trivial, while type (d) can also be reduced to type (a). However, since the operator in (d) is non-Hermitian, integrals of this type are not invariant with respect to the eight permutations of the labels—with respect to which (a), (b), and (c) are invariant. This means that the integral list for type (c) is twice as long as that of the other integrals. *In toto* we need hence 5 times as many two-electron integrals as in a conventional calculation.

Integrals that vanish for symmetry reasons are not computed. It would have been desirable not to compute integrals

that are smaller than a given threshold,<sup>11</sup> but this is hardly compatible with an effective vectorization on the CYBER 205. So we have renounced on this possibility, which is not too serious for the relatively small molecule studied in this paper.

All two-electron integrals can be expressed in terms of the generalized error function

$$F_m(x) = \int_0^1 t^{2m} e^{-xt^2} dt; \quad m = 0, 1, 2, 3, 4.$$

For  $x > 24$  we use the asymptotic expansion of  $F_m(x)$ , while the range  $0 < x < 24$  is divided into 15 360 intervals in each of which  $F_4(x)$  is represented as a third-order polynomial of  $x$ . The coefficients are stored. The  $F_m(x)$  with  $m < 4$  are evaluated via the recurrence relation

$$F_m(x) = \frac{1}{2m+1} \{e^{-x} + 2xF_{m+1}(x)\}.$$

This is only effective if a fast routine for  $e^{-x}$  is available. The standard CYBER 205 vector exponential is too slow. We have therefore followed an idea of Berg and Billoire<sup>12</sup> to store  $e^{-x}$  on a grid of  $x$  values and to evaluate  $e^{-x}$  as

$$e^{-x} \approx e^{-x-y} \{1 + y[1 + y(\frac{1}{2} + y^{\frac{1}{2}})]\},$$

where  $x+y$  is the closest grid point. This evaluation of  $F_m(x)$  vectorizes effectively with a performance of  $\sim 76$  MFLOPS on a CYBER 205 with two pipes.

Some data on computer times are given in Sec. IX.

### III. THE HYDROGEN AND LITHIUM HYDRIDE MOLECULES

The results for  $H_2$  and  $LiH$ —and for comparison  $He$  and  $Be$  are given in Table I.

The MP2-R12 results are rather close (within a few tenths of a millihartree) to those from the Gaussian geminal method and also close to the estimated exact values. As we

TABLE I. MP2 pair energies (negative in mhartree) of two- and four-electron systems.<sup>a</sup>

				MP2	MP2-R12 A	MP2-R12 B	GG <sup>b</sup>
He		$1s^2$	$^1S$	36.46	37.40	37.35	37.37
$H_2$	$R = 1.4 a_0$	$1\sigma_g^2$	$^1\Sigma_g^+$	33.36	34.23	34.17	34.11
Be		$1s^2$	$^1S$	39.12	40.37	40.34	40.34
		$1s2s$	$^1S$	3.17	3.24	3.21	3.25
			$^3S$	2.20	2.21	2.20	2.20
		$2s^2$	$^1S$	28.54	30.73	30.28	30.54
		$\Sigma$		73.03	76.56	76.04	76.35
LiH	$R = 3.015 a_0$	$1\sigma^2$	$^1\Sigma^+$	38.05	39.51	39.45	39.59
		$1\sigma 2\sigma$	$^1\Sigma^+$	1.37	1.48	1.41	1.47
			$^3\Sigma^+$	1.27	1.37	1.30	1.32
		$2\sigma^2$	$^1\Sigma^+$	28.73	30.41	30.00	30.40
		$\Sigma$		69.43	72.76	72.16	72.78

<sup>a</sup> Basis sets:  $[i,j,k/l,m,n]$  means, for example,  $is, jp, kd$  primitive Gaussians in the contraction  $ls, mp, nd$ ; without/: uncontracted, He: [16.10.6.3],  $H_2$ : [14.8.4.1/9.8.4.1], Be: [20.12.8.3], LiH: [14.7.4.1/11.7.4.1] for Li, [12.6.3.1/9.6.3.1] for H.

<sup>b</sup> Gaussian geminals, Ref. 13.

have found generally for atoms,<sup>2</sup> approximation A overestimates the second-order correlation energy somewhat, while approximation B underestimates it.

Our results with approximation A agree rather well with the Gaussian geminal (GG) results from the Monkhorst group.<sup>13</sup>

From separate calculations of LiH, Li<sup>+</sup>, and H<sup>-</sup> we can evaluate the binding energy of LiH with respect to Li<sup>+</sup> and H<sup>-</sup>. The results on four levels of calculation are:

SCF:7.156 eV, MP2:7.200 eV,

MP2-R12/A:7.217 eV, MP2-R12/B:7.211 eV.

Experimentally one gets 7.151 eV based on the dissociation energies of LiH:  $D_0^0 = 2.429$  eV,<sup>14</sup> the zero-point energy of 0.087 eV,<sup>14</sup> the ionization potential of Li  $I(\text{Li}) = 5.390$  eV,<sup>15</sup> and the electron affinity of H  $A(\text{H}) = -0.755$  eV. The SCF value is closest to experiment. All MP2 calculations overestimate the binding energy between the two ions slightly (by 0.05 to 0.06 eV). It remains to be seen what one gets from a treatment of electron correlation beyond MP2.

#### IV. THE TEN-ELECTRON MOLECULES HF, H<sub>2</sub>, NH<sub>3</sub>, AND CH<sub>4</sub>

In Table II the MP2-R12 energies in approximation A and B of the ten-electron systems Ne, HF, H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> in their ground states at the experimental equilibrium geometries are compared with values from the literature. A reliable estimate of the exact MP2 energy is available only for the Ne atom.

The difference between the MP2-R12/A and /B values is some measure of how close we are to basis saturation. This difference varies from slightly above 1% for Ne to almost 3% in the case of H<sub>2</sub>O. The distance to the exact MP2 results should be of the same order of magnitude, with the MP2-R12/A results probably closer and the MP2-R12/B values too small in absolute value. As we have already observed for atoms<sup>2</sup> the agreement with the extrapolations of Petersson *et al.*<sup>16-18</sup> is surprisingly good.

A discussion of the various pair contributions to the MP2 energy has been given in part II of this series<sup>2</sup> for the Ne atom. The analogous results for HF are found in Table III. Note that Table III is based on a much larger basis than Table II. From our results we conclude that the exact MP2 correlation energy of HF should lie between 380 and 382  $mE_h$ . For this molecule an interesting recent calculation is available for comparison.<sup>19</sup> It uses a method proposed by McCullough, that is only applicable to linear molecules, in which functions of the two elliptic coordinates  $\mu$  and  $\nu$  are expanded as

$$f(\mu, \nu) = \sum_k f_k(\mu) P_k(\nu)$$

with  $P_k(\nu)$  Legendre polynomials and  $f_k(\mu)$  evaluated numerically. Of course this expansion cannot be faster than the partial wave expansion in the atomic case, but going up to  $m_l = 3$  ( $\phi$  functions) an MP2 energy is obtained that differs only by 12–14  $mE_h \approx 3\%$  from what we regard as the basis set limit. To get the remaining 3% would, of course, be very hard, even with the method of Ref. 19, that is certainly very good in this case.

HF is the largest system for which a calculation with the Gaussian geminal method was performed,<sup>20</sup> although only for some selected pairs. The results of Ref. 20 are good for the  $1\sigma^2$  and  $2\sigma^2$  pairs, but poor for the  $3\sigma^2$  pair, as can be seen from Table III.

All pair energies for the molecules studied in this section (with the same basis sets as in Table II) are collected in Tables IV (a) and IV (b). It is most impressive how close HF and even H<sub>2</sub>O is to Ne, as far as both the total MP2 correlation energy and the individual pair contributions are concerned, while there are larger steps to NH<sub>3</sub> and CH<sub>4</sub>.

In the case of CH<sub>4</sub> the three functions that span the irrep.  $t_2$  (see Table V) are (unlike the three  $p$  functions in Ne) not symmetrically equivalent (only the third and fourth MO are equivalent). Unless one forces the three MOs to be equivalent in the SCF calculation (what has not been done here)

TABLE II. SCF and MP2 energies of the XH<sub>n</sub> molecules (ground states, experimental equilibrium geometries), negative in mhartree.<sup>a,b</sup>

	Ne	HF	H <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>
$E_{\text{SCF}}$	128 546.96	100 070.22	76 064.75	56 222.85	40 215.68
SCF limit <sup>c</sup>	128 547.01	100 070.82	76 067.5	56 226.	40 219.
MP2(conv.)	350.75	339.75	309.65	280.00	237.90
MP2-R12/A	388.55	378.84	360.04	320.65	271.82
MP2-R12/B	384.14	370.38	350.32	313.07	265.33
MP2 limit <sup>d</sup>	387.8				
CBS <sup>e</sup>	382.44	378.80	360.47	324.75	274.25

<sup>a</sup> Basis sets: Ne [16.10.7.3], HF [14.9.3.1] for F, [10.3.1] for H, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> [12.7.3.1/8.5.3.1] for O, N, and C [7.2/5.2] for H. Results for other basis sets are found for Ne in paper II, for H<sub>2</sub>O in Table VI, CH<sub>4</sub> in Ref. 5 and for HF in Table III.

<sup>b</sup> HF:  $R_e = 1.7328 a_0$ ; H<sub>2</sub>O:  $R_e = 1.80885 a_0$ ,  $\alpha = 104.52^\circ$ ; NH<sub>3</sub>:  $R_e = 1.91240 a_0$ ,  $\alpha = 106.72^\circ$ ; CH<sub>4</sub>:  $R_e = 2.05227 a_0$ .

<sup>c</sup> From Ref. 17, where original references are given.

<sup>d</sup> From paper II.

<sup>e</sup> Reference 17.

TABLE III. MP2 pair energies of the HF molecule (ground state,  $R_e = 1.7328 a_0$ ), negative in mhartree.

Pair	MP2 <sup>a</sup>	MP2 <sup>b</sup>	MP2-R12/A <sup>a</sup>	MP2-R12/A <sup>a</sup>	CBS <sup>c</sup>	GG <sup>d</sup>
	GTO	Semi-num.	GTO	GTO		
1 $\sigma^2$	36.91	38.89	40.63	40.56	40.42	40.2
1 $\sigma 2\sigma$	4.81	5.02	5.15	5.11	4.95	
2 $\sigma^2$	11.27	12.25	13.03	12.83	12.86	12.4
1 $\sigma 3\sigma$	4.91	5.17	5.26	5.21	5.16	
3 $\sigma 3\sigma$	25.24	27.58	29.08	28.51	29.65	
3 $\sigma^2$	26.87	28.25	29.33	28.98	29.02	27.2
1 $\sigma 1\pi$	12.33	13.02	13.24	13.10	12.76	
2 $\sigma 1\pi$	50.16	54.45	58.81	57.43	58.32	
3 $\sigma 1\pi$	83.48	87.11	89.86	88.64	88.01	
1 $\pi^2$	90.04	96.14	100.20	98.34	97.64	
$\Sigma$	346.03	367.88	384.59	378.71	378.8	

<sup>a</sup>Basis set [15.10.5.2] for F, [10.3.1] for H.<sup>b</sup>With the "seminumerical" McCullough method, Ref. 19.<sup>c</sup>"Complete-basis set extrapolation", Ref. 17.<sup>d</sup>Gaussian geminal method, Ref. 20.TABLE IV. (a) MP2-R12/A and (b) MP2-R12/B pair energies (negative in mhartree) of the ten-electron systems.<sup>a</sup>

Pair <sup>b,c</sup>	Ne	HF	H <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>
(a) 1-1	40.26	40.57	40.41	40.65	40.82
2-1	5.52	5.05	4.67	4.25	3.76
2-2	12.03	13.05	13.64	12.60	10.79
3-1		5.24	4.58		
3-2		28.87	29.53		
3-3		29.04	25.36		
4-1			5.84	4.02	
4-2			26.06	26.27	
4-3			41.06	32.00	20.52
4-4			25.46	23.26	21.35
5-1	7.25	6.25	6.34	5.77	3.42
5-2	29.08	28.78	28.28	23.56	22.21
5-3		44.17	39.74		
5-4	46.89	46.45	43.22	34.65	29.84
5-5	26.99	26.09	25.85	25.46	16.67
$\Sigma$	388.5	378.8	360.0	320.7	271.8
(b) 1-1	40.23	40.40	40.04	40.25	40.32
2-1	5.50	5.02	4.44	4.02	3.57
2-2	11.91	12.91	13.18	12.21	10.41
3-1		5.11	4.25		
3-2		28.40	28.73		
3-3		28.74	24.95		
4-1			5.38	3.70	
4-2			25.25	25.55	
4-3			40.59	31.56	20.14
4-4			24.81	22.86	20.92
5-1	7.23	6.00	5.45	5.23	3.18
5-2	28.59	27.82	27.07	22.78	21.51
5-3		43.44	38.92		
5-4	46.39	44.87	42.19	34.05	29.35
5-5	26.61	25.21	25.08	24.74	16.29
$\Sigma$	384.1	370.4	350.3	313.1	265.3

<sup>a</sup>Basis sets and geometries: as in Table II.<sup>b</sup>Contributions of equivalent pairs are only given once. In the case of CH<sub>4</sub> the three  $t_2$  MOs are not geometrically equivalent.<sup>c</sup>The symmetry classification of the MOs is found in Table V.

TABLE V. Classification of the MOs of the ten-electron systems.

	Ne	HF	H <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>
1	1s	1σ	1a <sub>1</sub>	1a <sub>1</sub>	1a <sub>1</sub>
2	2s	2σ	2a <sub>1</sub>	2a <sub>1</sub>	2a <sub>1</sub>
3	2p	3σ	1b <sub>2</sub>	1e	1t <sub>2</sub>
4	2p	1π	3a <sub>1</sub>	1e	1t <sub>2</sub>
5	2p	1π	1b <sub>1</sub>	3a <sub>1</sub>	1t <sub>2</sub>

they will usually not come out so, especially in a calculation with Gaussian lobes, where the five *d* functions are not equivalent.

For the example of H<sub>2</sub>O we have investigated the sensitivity of the MP2 results on details of the basis. The results are collected in Table VI.

One sees that on increasing the basis the MP2-R12 correlation energy does not reach its limit of  $\sim 360 mE_h$  in a monotonic way, unlike the way it does—*grosso modo*—in conventional MP2 calculations. One sees that from the first basis with *f* on O with  $N = 67$  to the largest basis with  $N = 106$  the MP2-R12 energy is nearly constant (variations of less than 1%), while without *f* on O but otherwise large basis sets the correlation energy is overestimated by 2%–3%. The second and the third basis with  $N = 44$  and 55, respectively, yield with MP2-R12 almost the exact MP2 correlation energy (in part due to a cancellation of errors) while with the same basis sets on conventional level only 73% or 79%, respectively, of the basis limit is obtained. Basis sets without *d* AOs on O, like the first one in Table VI, are not acceptable—because an essential completeness relation is

not satisfied (see appendix A of paper II) and one overshoots the correlation energy considerably. Note that for an accuracy of say 2 mhartree two *d* functions are necessary even on Hartree–Fock level.

In the case of CH<sub>4</sub> there was an interesting problem concerning its bond length  $r_e$ . The experimental value of 1.086 Å of Kuchitsu<sup>21</sup> has been questioned by W. Meyer, who got 1.091 Å from his CEPA calculation,<sup>22</sup> which could be regarded as a valid prediction since in other cases the agreement with reliable experimental values was within 0.001 Å. Various new experiments or new interpretations of old experiments, however, confirmed essentially Kuchitsu's value. Much more recently P. Siegbahn again found a theoretical value<sup>23</sup> very close to that of Meyer by a similar but more sophisticated approach. Handy<sup>24</sup> studied the same problem by MP2 and MP4 calculations paying special attention to the choice of the basis and found that the exponent of the polarization functions (mainly *p* on H) is rather critical. Handy's best MP2 value was  $r_e = 1.0829$  Å, while with Meyer's basis he got  $r_e = 1.086$  Å. Therefore, following Handy's suggestion, we calculated this quantity on MP2-R12 level, which should yield the basis set limit, with the result  $r_e = 1.0823$  Å. Combining this with Handy's estimate of the change from MP2 to MP4, a "recommended value" in agreement with the experimental one is obtained. This is also consistent with a very recent coupled-pair functional calculation of Siegbahn<sup>25</sup> with optimized basis sets.

For the ion CH<sub>5</sub><sup>+</sup> various structures are rather close in energy and one may wonder whether MP2-R12 results change anything with respect to conventional MP2 calculations. The results have been published elsewhere.<sup>5</sup> The order of relative stability of the various structures is not changed, but in MP2-R12 the C<sub>2v</sub> structure gets extremely close to the C<sub>s</sub> structure (difference  $\sim 0.2$  kcal/mol).

TABLE VI. SCF and correlation energy (negative in mhartree) of H<sub>2</sub>O at the experimental equilibrium geometry.

Basis					
O Atom	H Atom	N <sup>a</sup>	SCF	MP2 <sup>b</sup>	MP2-R12/A
[12.7/8.5]	[7/5]	33	76 023.7	188.2	548.6
[12.7.1/8.5.1]	[7.1/5.1]	44	76 056.8	262.4	361.0
[12.7.2/8.5.2]	[7.2/5.2]	55	76 063.1	283.2	361.5
[12.7.3/8.5.3]	[7.2/5.2]	60	76 063.6	294.0	368.9
[12.7.4/8.6.4]	[7.2/5.2]	68	76 063.9	301.6	368.2
[12.7.4/8.6.4] <sup>c</sup>	[7.2/5.2]	68	76 063.9	297.0	366.3
[12.7.5/9.7.5]	[10.5/7.5]	99	76 064.4	306.2	371.5
[12.7.3.1/8.5.3.1]	[7.2/5.2]	67	76 064.8	309.7	360.0
[12.7.3.1/8.7.3.1]	[7.2/5.2]	79	76 064.8	315.6	357.3
[12.7.4.1/8.7.4.1]	[7.2/5.2]	84	76 064.8	320.5	360.0
[12.7.4.1/8.7.4.1] <sup>c</sup>	[7.2/5.2]	84	76 065.0	315.8	358.4
[12.7.3.1/8.7.3.1]	[10.3.1/7.3.1]	93	76 065.6	318.5	358.8
[12.7.4.1/9.7.4.1]	[10.3.1/7.3.1]	99	76 065.7	323.6	362.3
[12.7.4.1/9.7.4.1] <sup>c</sup>	[10.3.1/7.3.1]	99	76 065.6	318.8	359.2
[12.7.4.2/9.7.4.2]	[10.3.1/7.3.1]	106	76 065.8	330.4	360.5

<sup>a</sup> Dimension of the basis (number of contracted Gaussians).

<sup>b</sup> Conventional.

<sup>c</sup> With one diffuse *d* function ( $\eta = 0.1$  instead of  $\eta = 8.1$ ).

## V. THE HOMONUCLEAR DIATOMIC SYSTEMS He<sub>2</sub>, N<sub>2</sub>, AND F<sub>2</sub>

### Description by localized vs canonical MOs

Conventional MP2 calculations are independent of whether one starts from canonical or localized MOs. The working equations are more complicated in terms of localized MOs, because the various pairs are coupled via the off-diagonal elements of the Fock operator. Such couplings make the MP2-R12 method more complicated in the localized than in the canonical case as well. Details are found in appendix A. Due to this coupling the solution has to be done iteratively, unless one first performs a canonical calculation and transforms to a localized one afterwards. So usually one does not gain anything in a localized description—except, as recently pointed out by Pulay<sup>26</sup> for large molecules, where contributions of pairs of distant LMOs can be neglected and the number of “significant” pairs is considerably reduced with respect to a calculation in terms of canonical MOs.

In the MP2-R12 method this invariance no longer holds. This is easily seen for the example of a pair of He atoms at a distance of  $10 a_0$  in Table VII. The essential information is contained in the coefficients  $c_{ij}$  for the various pairs. In the localized representation the coefficients  $c_{11}$  and  $c_{22}$  of the “intra” pairs for two electrons at the same He atom are rather close to the theoretical value 1 and very similar to the corresponding values for a single He atom in the same basis. A linear  $r_{12}$  factor is hence very efficient. For the “inter” pairs of the two electrons at different atoms—which describe the dispersion interaction—the variationally optimized coefficients are smaller than 0.1. An  $r_{12}$  factor is hence not very desirable for these pairs.

The factor  $r_{12}$  has to account for the behavior of the wave function at small interelectronic distances. For an inter pair a small interelectronic distance is very unlikely. The correct cusp is hence less important. On the other hand a linear factor  $r_{12}$  is certainly “wrong” for large distances between the electrons. In principle one ought to use a damping factor which tends to 0 for large  $r_{12}$  and to 1 for small  $r_{12}$ . It is, in fact, astonishing that such a damping factor is never needed in atomic calculations (as we have checked in test calculations). It appears that the exponential decay of atomic wave functions implies that the probability for large  $r_{12}$  also decays exponentially, such that the necessary damping is automatically taken care of.

This need no longer be so for molecules if one works with canonical and hence delocalized orbitals, while for localized molecular orbitals and intra-LMO correlation the situation should be similar as in atoms. For pairs of distant LMOs there is no automatic damping of the  $r_{ij}$  factor, so if one determines the coefficient  $c_{ij}$  of this factor by minimizing the Hylleraas functional one gets a small  $c_{ij}$ , because the “damage” of an  $r_{ij}$  term at large distance is more serious than what one gains at small  $r_{ij}$ .

For He<sub>2</sub> at large internuclear distance the result obtained in a localized representation is rather reasonable. One overestimates the attractive interaction (at least in approximation A). This is so small that the inaccuracy introduced by the completeness interactions is not negligible compared to the small interaction energy.

TABLE VII. MP2-R12/A pair energies (negative in mhartree) of a system of two He atoms at a distance of  $10 a_0$ . Comparison of the canonical and the localized representation.

Pair		Canonical		Localized	
		$E_{ij}$	$c_{ij}$	$E_{ij}$	$e_{ij}$
1-1	<sup>1</sup> Σ	18.6574	0.879	37.3306	0.885
2-1	<sup>1</sup> Σ	37.3306	0.885	0.0005	0.087
	<sup>3</sup> Σ	0.0014	0.087	0.0014	0.087
2-2	<sup>1</sup> Σ	18.6599	0.879	37.3306	0.885
	$E^{(2)}$	74.6493		74.6631	

<sup>a</sup> Basis [16.8.4].

If we now look at He<sub>2</sub> in the canonical representation, we find no difference for the triplet pair. Of course, this pair is uniquely determined and ( $a$  and  $b$  are the LMOs)

$$\frac{1}{\sqrt{2}} \{a(1)b(2) - b(1)a(2)\} \\ = \frac{1}{\sqrt{2}} \{\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)\}.$$

For the singlet pairs the situation is more complicated

$$\sigma_g(1)\sigma_g(2) = \frac{1}{2} \{a(1)a(2) + b(1)b(2) \\ + a(1)b(2) + b(1)a(2)\}, \\ \sigma_u(1)\sigma_u(2) = \frac{1}{2} \{a(1)a(2) + b(1)b(2) \\ - a(1)b(2) - b(1)a(2)\}, \\ \frac{1}{\sqrt{2}} \{\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)\} \\ = \frac{1}{\sqrt{2}} \{a(1)a(2) - b(1)b(2)\}.$$

The canonical singlet interorbital pair describes hence pure intraorbital correlation of LMOs, while singlet intra pair functions are mixtures of inter-LMO and intra-LMO situations. Consequently the factor  $c_{11} = c_{22}$  will turn out to be a compromise between those for intra and inter LMO pairs. In view of the large magnitude of the intra LMO correlation energy this part will dominate and force the inter LMO pair part to have a much too large  $r_{ij}$  term. This raises the energy by  $\sim 14 \mu E_h$ , which is much if one is interested in dispersion energies, that are smaller by a factor 10, but which is a very small fraction (0.02%) of the MP2 correlation energy.

The computation of the dispersion interaction between two He atoms from a supermolecule calculation has always been a hard challenge because the dispersion energy is a very small fraction of the overall correlation energy. Even for this kind of problem the MP2-R12 method is very helpful. With MP2-R12/B we get (Table VIII) an interaction energy of  $-2.0$  and  $-33.9 \mu\text{hartree}$  for  $R = 10 a_0$  and  $5.6 a_0$  (equilibrium distance), respectively, compared to  $-1.4$  and  $-17.7 \mu\text{hartree}$  from conventional MP2 in the same basis. The exact values are close to  $-1.6$  and  $-35 \mu\text{hartree}$ , respectively. MP2-R12/B appears to do here quite well.

TABLE VIII. The interaction energy (in  $\mu$  hartrees) of two He atoms at two distances.<sup>a</sup>

	$R = 5.6 a_0^c$	$R = 10.0 a_0$	He atom <sup>b</sup>
SCF	29.2	0.0	
MP2	-17.7	-1.4	35 161
MP2-R12/A	-47.1	-2.1	37 331
MP2-R12/B	-33.9	-2.0	37 131

<sup>a</sup>Basis as in Table VII, localized representation.<sup>b</sup>Correlation energy of a single He atom in the same basis (also in  $\mu$  hartrees).<sup>c</sup>At this distance a counterpoise correction lowers the interaction energy in absolute value by  $2 \mu E_h$ , both on MP2 and MP2-R12 level.

The comparison localized vs canonical of the MP2-R12 calculation of  $F_2$ , at its equilibrium distance is displayed in Tables IX and X. The total MP2-R12 correlation energies differ by less than 0.01%, (Table IX), but somewhat larger relative changes are found if one compares just the contributions of the  $K$ -shells (Table X), where qualitatively a picture very similar to the  $He_2$  system (Table VI) is found. However, the difference of  $4 mE_h$  of the total  $K$ -shell contribution canonical vs localized has its origin mainly in the fact that the localization procedures mixes some amount of valence MOs into the core. In fact almost the same difference is found in a conventional MP2 calculation.

The MP2-R12 pair energies for the  $N_2$  molecule in its ground state are found on Table XI. We have only considered the valence MOs. For these it does not matter whether or not one localizes them (at least as long as one does not include the  $K$ -shell AOs in the localization procedure). Here the canonical approach is more convenient.

We have compared two basis sets I and II and with the large basis the schemes MP2-R12/A and MP2-R12/B. Unfortunately (but in agreement with general trends) the two

TABLE IX. MP2-R12/A pair energies of  $F_2$  in a canonical and a localized representation.<sup>a</sup>

Pair	Mult.	Canonical	Localized	Localized
$c^2$	(2)		42.27	
$c-c''$	(1)		0.01	
Core		80.99		84.54
$b-c$	(2)		3.10	
$p-c$	(6)		5.55	
$p-c''$	(6)		0.77	
Core/valence		42.70		44.12
$b^2$	(1)		27.88	
$p-b$	(6)		23.89	
$p^2$	(6)		25.51	
$p-p'$	(6)		29.29	
$p-p''$	(9)		11.06	
Valence		603.97		599.58
$\Sigma$		727.66		728.24

<sup>a</sup>Basis [14.9.3.1].  $c$ : core;  $b$ : band;  $p$ : lone pair;  $p-p'$ : two lone pairs at the same atom;  $p-p''$ : at different atoms.TABLE X. MP2-R12/A pair energies of the core MOs of  $F_2$  in a canonical and a localized representation.

Pair		Canonical		Localized	
		$E_{IJ}$	$c_{IJ}$	$E_{IJ}$	$c_{IJ}$
1-1	$^2\Sigma$	20.223	0.77	42.265	0.79
2-1	$^1\Sigma$	40.540	0.79	0.003	0.03
	$^3\Sigma$	0.000 13	0.01	0.007	0.01
2-2	$^1\Sigma$	20.226	0.77	42.265	0.79
	Sum	80.99		84.54	

<sup>a</sup>Basis as in Table IX.

calculations (A and B) have not converged to the same value (they differ by about 3%). Our experience let us expect that the exact basis set limit is between approximation A and B, and—for GTO basis sets—closer to approximation A. Our estimate of the basis set limit of the MP2 energy of  $N_2$  at its equilibrium distance is hence  $-418 \pm 3 mE_h$ . This is consistent with an extrapolation from conventional calculations with very large basis sets.<sup>27</sup>

## VI. POTENTIAL CURVE OF THE $Be_2$ MOLECULE

The  $Be_2$  molecule with its unusually weak chemical bond has been a great challenge to computational quantum chemistry, and there are few examples comparable to  $Be_2$  for which the theoretical results are extremely sensitive to the methods used, and also to the basis sets. For a review see Ref. 28.

It appeared hence worthwhile to apply the MP2-R12 method in order to construct a potential curve that should be close to the basis set limit of MP2. The results are given in Table XII together with SCF results and conventional MP2 values in the same basis. Again the agreement with the CBS extrapolation by Petersson *et al.*<sup>29</sup> is surprisingly good. The plot on Fig. 1 (in which also preliminary MP3-R12 results are included) clearly shows how much the potential curve is changed by inclusion of the  $r_{12}$  term. The next step to perform would be to study the limit of excitation level in a correlation treatment.

## VII. ACETYLENE

We have performed MP2-R12 calculations on acetylene  $C_2H_2$  in its ground state at equilibrium geometry, because a rather sophisticated conventional MP2 calculation, using a direct MP2 program has recently been published by Saebø and Almlöf.<sup>6</sup> Our results are displayed in Table XIII together with those of Ref. 6. These latter results are roughly in the middle between our MP2 and MP2-R12 values. While with our basis a conventional MP2 calculation yields 82.4% of the estimated basis set limit (i.e., the MP2-R12 result), the basis of Ref. 6 allows to account for 93.7%. However, the basis of Ref. 6 is more than 3 times as larger as our basis. While Saebø and Almlöf<sup>6</sup> needed 9000s on a CRAY 2 our MP2-R12 calculation required only 1300s on a CYBER 205



TABLE XI. MP2 valence pair energies of the  $N_2$  ground state, negative in mhartree, at the equilibrium distance ( $R = 2.07 a_0$ ).

Pair <sup>a</sup>	MP2 <sup>b</sup> Basis I <sup>c</sup>	MP2 <sup>b</sup> Basis II <sup>d</sup>	MP2-R12/A Basis I <sup>c</sup>	MP2-R12/A Basis II <sup>d</sup>	MP2-R12/B Basis II <sup>d</sup>
$2\sigma_g^2$	12.05	13.50	17.65	16.69	16.04
$2\sigma_g 2\sigma_u$	9.25	9.59	10.30	10.40	10.24
$2\sigma_u^2$	15.32	15.86	17.82	17.66	17.37
$2\sigma_g 3\sigma_g$	12.98	14.52	18.06	16.92	16.27
$3\sigma_g 2\sigma_u$	25.63	26.94	30.80	30.57	29.81
$3\sigma_g^2$	15.17	15.90	18.05	17.79	17.30
$2\sigma_g 1\pi_u$	48.27	51.63	66.27	62.71	59.15
$2\sigma_u 1\pi_u$	49.35	51.17	55.25	55.19	53.97
$3\sigma_g 1\pi_u$	61.06	62.92	68.31	67.10	65.73
$1\pi_u^2$	113.80	115.69	129.98	128.02	123.40
$\Sigma^e$	362.88	377.72	432.49	423.05	409.28
% of 418	86.8	90.4	103.5	101.2	97.9

<sup>a</sup>Sums of the respective singlet and triplet pairs.

<sup>b</sup>Conventional MP2.

<sup>c</sup>Basis I: [14.10.4]; 14s 10p from Huzinaga and M. Klobukowski, *Theochem.* **44**, 1 (1988). 4d with  $\eta = 0.4$ ; 1.1; 3.1; 9.0;  $E(\text{SCF}) = -108.989 53 E_h$ .

<sup>d</sup>Basis II: [14.10.4.1] as basis I with an additional *f* function with  $\eta = 3.0$ ;  $E(\text{SCF}) = -108.991 33 E_h$ .

<sup>e</sup>Sums of the valence pairs.

(which should be slower by a factor 2–4). From a comparison with our  $N_2$  calculation we conclude that our result may overestimate the exact basis limit by 10 to 15  $mE_h$ . In this case the result of Ref. 6 would differ by only  $3 \pm 1\%$  from the basis set limit.

An MP2-R12 study of  $C_2H_4$  and the ions  $C_2H_3^+$ ,  $C_2H_5^+$  in their classical and nonclassical structures has been published elsewhere.<sup>5</sup>

TABLE XII. Potential curve of the  $Be_2$  molecule in MP2 and MP2-R12/A approximation.<sup>a</sup>

$R/a_0$	SCF	MP2	MP2-R12/A
4.50	13.944	1.309	-1.293
4.60	12.499	0.684	-1.781
4.70	11.261	0.223	-2.078
4.75	10.708	0.042	-2.189
4.80	10.193	-0.111	-2.287
4.85	9.713	-0.240	-2.349
4.90	9.265	-0.349	-2.390
4.95	8.844	-0.440	-2.422
5.00	8.450	-0.516	-2.437
5.05	8.080	-0.578	-2.442
5.10	7.731	-0.630	-2.438
5.20	7.089	-0.706	-2.403
5.30	6.513	-0.756	-2.358
5.50	5.518	-0.805	-2.240
6.00	3.661	-0.817	-1.955
6.50	2.391	-0.791	-1.750
7.00	1.521	-0.739	-1.599
7.50	0.924	-0.662	-1.474

<sup>a</sup>The entries are energy differences in mhartree with respect to two isolated Be atoms in the same basis GTO basis [14.9.3].

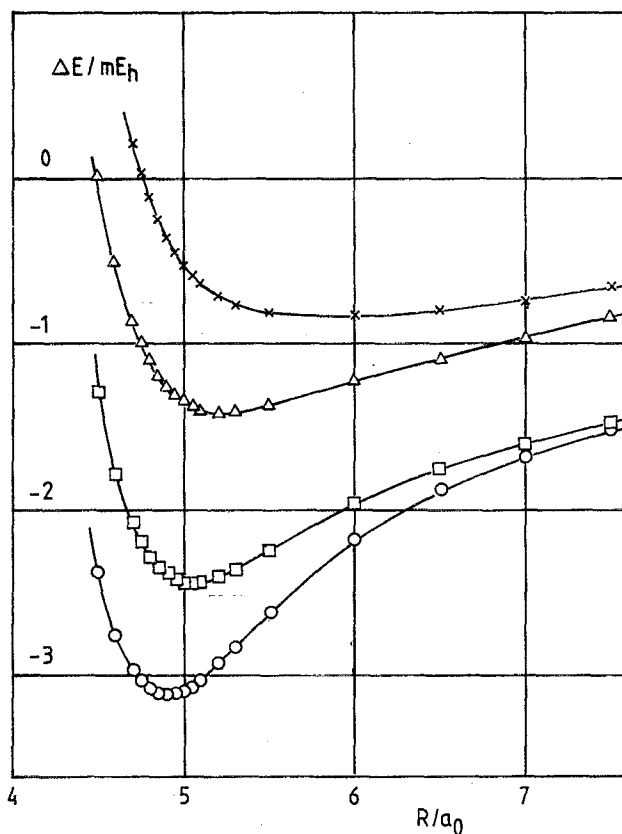


FIG. 1. Potential curves of the  $Be_2$  molecule from MP2 and MP3 calculations in a localized representation with a [14.9.3] GTO basis.  $\times$ : conventional MP2;  $\square$ : MP2-R12;  $\triangle$ : conventional MP3;  $\circ$ : MP3-R12.

TABLE XIII. MP2-pair energies of acetylene ( $C_2H_2$ ) ground state negative in mhartree, at the equilibrium geometry.<sup>a</sup>

Pair <sup>c</sup>	MP2 <sup>b,c</sup> Ref. 6	MP2 <sup>b,d</sup>	MP2-R12/A <sup>c</sup>
$2\sigma_g^2$	9.83	12.44	14.45
$2\sigma_g 2\sigma_u$	7.75	8.82	9.15
$2\sigma_u^2$	13.37	15.28	16.19
$2\sigma_g 1\pi_u$	41.49	50.94	57.33
$2\sigma_u 1\pi_u$	31.78	35.58	35.83
$1\pi_u^2$	94.81	102.97	109.84
$2\sigma_g 3\sigma_g$	12.06	15.43	17.05
$2\sigma_u 3\sigma_g$	24.62	28.13	29.62
$1\pi_u 3\sigma_g$	44.91	49.38	51.26
$3\sigma_g^2$	13.83	15.70	16.41
$\Sigma$	294.45	334.67	357.13

<sup>a</sup> $R_{CC} = 2.2796 a_0$ ;  $R_{CH} = 2.0037 a_0$ .<sup>b</sup>Conventional MP2.<sup>c</sup>GTO basis C: [12.7.3/8.5.3] H: [7.2/5.2], number of GTOs: 98; SCF energy  $-76.85066 E_h$ .<sup>d</sup>GTO basis. C: [13.8.6.4.2] H: [8.6.4], number of GTOs: 318; SCF energy  $-76.85512 E_h$ .<sup>e</sup>Sum over singlet and triplet pairs.

### VIII. A TRANSITION METAL COMPOUND: CuH

In order to show that MP2-R12 calculations are also possible for molecules containing transition metal atoms we have performed a calculation of CuH at the distance  $R_e = 2.764 a_0$ .

The results for the pairs that essentially belong to the  $Cu^+$  core have already been documented in paper II of this series.<sup>2</sup> On Table XIV we give the pair energies for those pairs that involve the bond. The total contributions of these pairs to the MP2 energy is 97 mhartree on conventional MP2 level and 131 mhartree from an MP2-R12/A calculation. Taking care of the change of the correlation energy of the core on molecule formation (MP2: 19  $mE_h$ , MP2-R12: 31

TABLE XIV. Pair correlation contributions (negative, in mhartree) in CuH of the pairs that involve the CuH bond orbital (b).

		MP2	MP2-R12/A
1s	b	0.03	0.10
2s	b	0.48	0.70
3s	b	2.64	3.90
2p	b	2.42	3.00
3p	b	12.74	17.26
3d	b	63.98	88.04
$b^2$		14.76	18.39
$\Sigma$		97.03	131.40
Core	in CuH	1182.24	1627.92
Total		1279.27	1759.32
Free	$Cu^+$	1201.66	1658.64
Free	$H^-$	26.70	28.94
CuH	$-(H^- + Cu^+)$	50.91	71.74

Basis as in paper II of this series (Ref. 2).

$mE_h$ ) and of the correlation energy of  $H^-$  we predict a change of the correlation energy from  $Cu^+ + H^-$  to CuH of 51  $mE_h$  (MP2) or 72  $mE_h$  (MP2-R12/A).

Like in the case of LiH (see Sec. III) we can compare various calculations of the binding energy of CuH with respect to  $Cu^+$  and  $H^-$ . The experimental value of 9.82 eV results from  $D_e(CuH) = 2.85$  eV,<sup>14</sup>  $I(Cu) = 7.72$  eV,  $A(H) = -0.76$  eV. On various theoretical levels we get SCF: 8.10 eV, MP2: 9.49 eV, MP2-R12/A: 10.05 eV. The correlation effect is now almost 2 eV (compared to 0.05 eV for LiH). Of the theoretical results the MP2-R12/A value (we have not done/B) is closest to experiment (larger by 0.2 eV). Again it remains to be seen what one gets beyond MP2. Of course, relativistic effects would then also have to be included.

### IX. COMPUTER TIMES

To illustrate the cost of MP2-R12 calculations, some computer times are listed in Table XV. Three calculations from which the results are presented in this paper (and in paper II of this series in the case of Ca) are supposed to represent the current usage of our program. Because of the completely different symmetries of the three systems considered, it is hard to compare the individual timings, and some remarks may be helpful: (a) the time needed for integral evaluations trivially is the most time consuming step if many lobes are used in the basis, while the other times depend on the number of basis functions and correlated orbitals. (b) Since the Fock matrix of Ca and  $N_2$  is strongly symmetry-blocked, the corresponding eigenvectors are very sparse, which results in better timing for the MP2 calculations in comparison with  $CH_4$  where this is not the case in a basis of Gaussian lobes. (c) MP2-R12/B calculations need 3 times as much computer time as approximation A. But in doing MP2-R12/B calculations, an MP2-R12/A calculation is done first, which then can be seen as an intermediate result.

### X. CONCLUSIONS

The idea to include linear  $r_{12}$  terms in the wave functions, together with the necessary completeness insertions to make the theory feasible, has turned out to be successful. In the framework of Møller–Plesset second-order perturbation theory (MP2-R12) using Gaussian basis sets one is able to get correlation energies that differ by at most a few percent from the estimated basis set limit. The error in the correlation energy as compared to conventional MP2 calculations in the same basis is reduced by a factor of the order 10, while the computational effort only increases by a factor around 5. In principle the method is not limited to small molecules. However, the basis sets must not be too small; not fulfilling certain completeness conditions may lead to unacceptable results. For each first-row or second-row atom the basis must contain a few  $d$  AOs and if possible an  $f$  AO.

The MP2-R12 method can be applied successfully to problems of structural chemistry, e.g., to the problem of the bond length of  $CH_4$ , the relative stability of carbonium ions or the potential curve of  $Be_2$ , or even the binding energy of CuH. We have not pushed applications of this type too far,

TABLE XV. Computer times in CPU seconds.<sup>a</sup>

	Ca	N <sub>2</sub>	CH <sub>4</sub>
Basis X:	[20.15.8.2]	[14.10.4.1]	[12.7.3.1/8.5.3.1]
H:			[7.2/5.2]
Number of contracted GTOs	119	142	89
Number of lobes	350	388	231
Memory needed for two-electron integrals in Mbyte	191	384	232
Number of correlated orbitals	10	5	5
Integral evaluation	3547	5472	2410
SCF calculation	83	196	105
MP2-R12/A <sup>b</sup>	626	891	1211
MP2-R12/B <sup>c</sup>	1384	1786	2279
Total	5640	8345	6005

<sup>a</sup> On a CYBER 205 with two pipes.

<sup>b</sup> Conventional MP2 included, which is not separately programmed.

<sup>c</sup> Using results of the MP2-R12/A calculation.

since definite answers would require to abandon the MP2 approach and to use some kind of coupled-cluster method. Work on these lines is in progress.

The MP2-R12 method can be formulated in a canonical or in a localized representation. For weakly interacting localized units, e.g. the He<sub>2</sub> system, the localized representation is by far superior, while in ordinary molecules there is not much difference between the two representations.

The MP2-R12 method has been proposed in two versions, approximations A and B. Theoretical considerations as well as the experience with atoms strongly indicate that approximation B is better, insofar as with increasing basis size it converges faster to the basis set limit, and as practically it provides upper bounds to the MP2 energy. In the molecular calculations presented here the MP2-R12/A and MP2-R12/B correlation energies differ by a few percent with the results of approximation A usually closer to the estimated basis set limits. In special cases like that of the He<sub>2</sub> system approximation B is definitely preferable.

## ACKNOWLEDGMENTS

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## APPENDIX A

### The MP2 method in a localized representation

The derivation given in Paper I<sup>1</sup> is not limited to the case that the occupied orbitals are canonical. In fact Eq. (I.7.3), is valid even if the Fock matrix  $f_{ij}^p$  is nondiagonal. Only the simplification (I.7.4) then no longer holds. As far as the conventional MP-2 part  $F_1$  given by Eq. (I.7.3b) is concerned, its minimization with respect to the coefficients  $d_{ij}^{ab}$  now leads to a linear system of equations in which the various  $d_{ij}^{ab}$  are coupled. This can be solved iteratively in ne-

glecting the coupling terms in the first iteration. For the molecules studied in this paper it has become easier to first compute the  $d_{ij}^{ab}$  in the canonical representation, i.e., from Eq. (I.7.6a) and then to transform them to the localized representation.

In  $F_2$  given by Eq. (I.7.3c) coupling terms also arise in addition to the diagonal terms given by Eq. (I.7.4b), namely couplings between pairs that have one common index, as given by Eq. (1.5.5) in either standard approximation.

The extra term to  $F_2$  is hence

$$\frac{1}{4} \sum_I \sum_{j \neq l} \left\{ (\bar{r}^2)_{il}^{II} - \frac{1}{2} \bar{r}_{il}^{pq} \bar{r}_{pq}^{II} \right\} f_j^I c_{il}^{II}$$

or in spinfree formulation

$$\frac{1}{4} \sum_I \sum_{j \neq l} \left\{ \left[ (r^{+2})_{il}^{II} - \sum_{P < Q} r_{il}^{PQ} r_{PQ}^{II} \right] c_{il}^{II} + c_{il}^+ (1 + \delta_{IJ}) \right. \\ \left. \times (1 + \delta_{IL}) + 3 \left[ (\bar{r}^2)_{il}^{II} - \sum_{P < Q} \bar{r}_{il}^{PQ} \bar{r}_{PQ}^{II} \right] c_{il}^{II} - c_{il}^- \right\} f_j^I.$$

Minimization of  $F_2$  with respect to the  $c_{ij}^{\pm}$  leads to a linear system of equations from which the optimum  $c_{ij}^{\pm}$  can be obtained.

## APPENDIX B

### On the choice of the orbital exponents

In appendix B of paper II<sup>2</sup> some arguments were given how to choose the STO basis functions of higher angular momentum in order to account for a large part of the correlation energy and to satisfy the required completeness relations.

In analogy to Eq. (II.B.1) we get for a one-center overlap integral  $S$  between two Gaussians with orbital exponents  $\beta_1, \beta_2$  and principle quantum numbers  $n_1, n_2$ , respectively:

$$S = \frac{\Gamma([n_1 + n_2 + 1]/2)}{(\beta_1 + \beta_2)^{(n_1 + n_2 + 1)/2}} \\ \times \frac{(2\beta_1)^{(2n_1 + 1)/4} (2\beta_2)^{(2n_2 + 1)/4}}{[\Gamma(n_1 + \frac{1}{2}) \Gamma(n_2 + \frac{1}{2})]^{1/2}}. \quad (\text{B1})$$

This reaches its maximum  $S = 1$  for  $n_1 = n_2$  and  $\beta_1 = \beta_2$ . For  $n_1, n_2$ , and  $\beta_1$  fixed,  $S(\beta_2)$  reaches its maximum for

$$\beta_2 = \beta_1 \frac{2n_2 + 1}{2n_1 + 1} \quad (\text{B2})$$

This happens to be exactly the same relation as for STOs [Eq. (II.B.2)]. Insertion of Eq. (B2) into Eq. (B1) and use of the Stirling formula leads to

$$S_{\max} \approx [(2n_1 + 1)(2n_2 + 1)]^{1/4} (n_1 + n_2 + 1)^{-1/2} \quad (\text{B3})$$

again exactly as in the case of STOs.

Consider then an exchange-type integral like Eq. (II.B.7). Instead of Eq. (II.B.8) we get

$$\begin{aligned} & \frac{1}{k} \int_0^\infty r^{2(n_a + n_b)} e^{-2(\beta_a + \beta_b)r^2} dr \cdot N_a^2 \cdot N_b^2 \\ &= \frac{1}{k} \frac{\Gamma(n_a + n_b + \frac{1}{2})}{[2(\beta_a + \beta_b)]^{n_a + n_b + 1/2}} \\ & \quad \frac{(2\beta_a)^{n_a + 1/2} (2\beta_b)^{n_b + 1/2}}{\Gamma(n_a + \frac{1}{2}) \Gamma(n_b + \frac{1}{2})}. \end{aligned} \quad (\text{B4})$$

Stationarity with respect to variation of  $\beta_b$  is reached if

$$\beta_b = \frac{n_b + \frac{1}{2}}{n_a} \beta_a \quad (\text{B5})$$

again exactly as in the case of STOs [see Eq. (II.B.10)].

Like in paper II Appendix B we want to maximize products

$$\begin{aligned} & \langle a(1)a(2) \left| \left( \frac{1}{r_{12}} \right)_k \right| b(1)b(2) \rangle \\ & \times \langle b(1)b(2) | (r_{12})_k | a(1)a(2) \rangle, \end{aligned} \quad (\text{B6a})$$

$$\begin{aligned} & \langle a(1)b(2) \left| \left( \frac{1}{r_{12}} \right)_k \right| c(1)d(2) \rangle \\ & \times \langle c(1)d(2) | (r_{12})_k | a(1)b(2) \rangle \end{aligned} \quad (\text{B6b})$$

with respect to variation of  $\beta_b$  in the first case and  $\beta_d$  in the second one. The result is

$$\beta_b = \beta_a \frac{2n_b + 1}{2n_a + 1}, \quad (\text{B7a})$$

$$\beta_d = (\beta_a + \beta_b + \beta_c) \frac{2n_d + 1}{2n_a + 2n_b + 2n_c + 3}. \quad (\text{B7b})$$

Since in GTO calculations we always have

$$n = l + 1 \quad (\text{B8})$$

then for a given basis functions with  $l_a$  and  $\beta_a$  we need a partner with  $l_b$  and

$$\beta_b = \beta_a \frac{2l_b + 3}{2l_a + 3}. \quad (\text{B9})$$

We have first found the optimum orbital parameters for "polarization functions" empirically, but the agreement with

Eq. (B9) and  $\beta_a$  the most important exponent in a Hartree-Fock calculation is striking.

From these consideration it is obvious that, e.g., for Ne we need in addition to the Hartree-Fock basis at least one  $p$  function for  $1s$  and one (or rather 2 or 3 of them)  $d$  function for  $2p$ ; (the  $d$  functions for  $1s$  and  $2s$  are less important), as well as one  $f$  function for  $2p$ ; for Ar again one  $p$  function for  $1s$  at least two  $d$  functions for  $2p$  and  $3p$  and two  $f$  functions for  $2p$  and  $3p$  with the latter more important than the former.

Methane should be analogous to Ne, but the  $f$  functions are less necessary since  $p$  functions on H simulate  $f$  functions around Ne to some extent.

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