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Citation: *The Journal of Chemical Physics* **94**, 2002 (1991); doi: 10.1063/1.459922

View online: <http://dx.doi.org/10.1063/1.459922>

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

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(Received 17 July 1990; accepted 9 October 1990)

The MP2-R12 method in approximations A and B as outlined in part I of this series is applied to the ground states of the closed-shell atoms He, Be, Ne, Mg, Ar, Ca, Cu<sup>+</sup>, Zn<sup>2+</sup>, and Kr, in terms of both STO and GTO basis sets. For He, Be, and Ne the partial wave increments of the various pairs are documented and compared with their conventional counterparts. The fast convergence of the partial wave increments, that go as  $(l + \frac{1}{2})^{-8}$  in the MP2-R12/B scheme, is demonstrated. From the MP2-R12 calculations more accurate estimates of the exact MP2 energies are possible than from the conventional partial wave expansion. The actually calculated values differ generally by a fraction of a 1% from the estimated basis sets limits if STO basis sets with  $l < 5$  (in some cases  $l < 6$ ) are used, while errors of typically 1% are obtained with GTO basis sets and  $l < 3$ .

## I. INTRODUCTION

The problem of the slow convergence of the conventional basis-set expansion method in quantum chemistry and theoretical atomic physics can be overcome if one uses wave functions that contain terms linear in the interelectronic coordinates  $r_{ij}$ , and which are hence able to describe the correlation cusp<sup>1</sup> correctly. It has been shown recently<sup>2,3</sup> that it is imperative for a rapidly convergent expansion that the basis is able to describe the singularities of the wave function.

The general theory has been outlined in part I of this series.<sup>4</sup> We now report on the results of atomic calculations, while a companion paper<sup>5</sup> deals with molecules. For this first systematic investigation of the linear  $r_{12}$  method, the frame of second-order Møller–Plesset perturbation theory (MP2) has been used. This approach will be referred to as MP2-R12. We have chosen the MP2 frame because (restricted) MP2 is a well-defined first step in a hierarchy of methods to account for electron correlation in atoms or molecules. (The next steps need not be MP to higher orders, but can, e.g., be coupled-cluster (CC) methods of increasing sophistication). The slow convergence of CI-type calculations (including MP, CC, etc.) has two reasons, one is the incompleteness of the one-electron basis (and it is this which can be overcome by the linear  $r_{12}$  method), the other the truncation of the excitation level or the order of perturbation theory. In order to make clear statements concerning the basis incompleteness problem we do not want to mix the two aspects.

Two independent computer programs have been implemented, one especially for atoms using STO basis sets and taking full advantage of the standard angular momentum algebra (we shall refer to this as the “atomic program”), and another one (the “molecular program”) mainly designed for molecules in a basis of Gaussian lobe functions, which is, of course, also applicable to atoms.

A short description of special features of the method in the atomic case and of the “atomic computer program” will

be given in Sec. II. We then start with a systematic report on the neutral closed-shell atoms from He to Kr (taking Zn<sup>2+</sup> and Cu<sup>+</sup> rather than Ni for a  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  configuration). For details of the molecular program which will also be applied here, the reader is referred to part III.<sup>5</sup>

## II. METHOD AND COMPUTER PROGRAMS

The MP2-R12 method has been presented in detail in paper I of this series,<sup>4</sup> especially in Sec. VII. The main concept has also been outlined previously<sup>6–8</sup> such that we can be brief here as far as the general ideas are concerned. Only some details specific for the atomic case need to be given.

We want to minimize the Hylleraas functional for the second-order correlation energy

$$F(\psi^{(1)}) = 2 \operatorname{Re} \langle \psi^{(1)} | V - E_1 | \phi \rangle - \langle \phi | H_0 - E_0 | \psi^{(1)} \rangle \geq E^{(2)} \quad (2.1)$$

with  $\phi$  the closed-shell Hartree–Fock function and  $\psi^{(1)}$  the first-order wave function. This decouples into a sum of pair contributions

$$F(\psi^{(1)}) = \sum_{i < j} f(w_{ij}) \quad (2.2)$$

$$f(w_{ij}) = 2 \operatorname{Re} \langle [ij] | r_{12}^{-1} | w_{ij}(1,2) \rangle + \langle w_{ij}(1,2) | F(1) + F(2) - \epsilon_i - \epsilon_j | w_{ij}(1,2) \rangle \quad (2.3)$$

$$[pq] = 2^{-1/2} [\varphi_p(1 - \varphi_q(2)) - \varphi_q(1) \varphi_p(2)] \quad (2.4)$$

with  $[ij]$  and  $w_{ij}$  the unperturbed and first-order pair functions, respectively. We make the ansatz

$$w_{ij}(1,2) = \frac{1}{2} c_{ij} \{1 - P(1)\} \{1 - P(2)\} r_{12} [ij] + \omega_{ij}(1,2), \quad (2.5)$$

$$P(1) = \sum_k |\varphi_k(1)\rangle \langle \varphi_k(1)|; \quad \omega_{ij}(1,2) = \sum_{a < b} d_{ij}^{ab} [ab], \quad (2.6)$$

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

The projectors  $P$  in Eq. (2.5) are necessary to make the first-order function  $\psi^{(1)}$  strongly orthogonal to  $\phi$ . It has turned out advantageous to orthogonalize the  $r_{12}$  part to all double excitations that are describable in the given basis. This can be achieved by changing the projectors in Eq. (2.5) to projectors  $\tilde{P}$  for the given basis. The  $r_{12}$  term then takes care of the short-range correlations that are not accounted for by this basis. For details see paper I and also Ref. 8.

In principle  $F(\psi^{(1)})$  could be evaluated and minimized exactly. However, this would imply that difficult three- and four-electron integrals like

$$\int \phi(1,2,3)r_{12}r_{23}^{-1}r_{13} d\tau_1 d\tau_2 d\tau_3 \quad (2.7)$$

have to be evaluated. Even more serious than the difficulty to evaluate such integrals is their large number ( $\sim N^6$  or  $\sim N^8$ ). We have therefore introduced approximations, by which the evaluation of "difficult" integrals is avoided. These approximations have in common that they become exact in the limit of a complete basis, and they guarantee that the *basis set limit is reached much faster* than in conventional CI calculations. Two standard approximations, referred to as A and B as explained in part I<sup>1</sup> in Sec. V will be used and compared.

For atoms the errors due to truncation of the basis at a given angular quantum number  $l$  go in a conventional CI calculation as  $\sim (l+1)^{-3}$ , in our scheme B as  $\sim (l+1)^{-7}$ , while in scheme A small contributions  $\sim (l+1)^{-5}$  are present. The price to pay for this faster convergence is that the upper bound property of  $F(\psi^{(1)})$  is lost. We do not necessarily approach  $E^{(2)}$  from above. It appears however, that only approximation A has a tendency to approach  $E^{(2)}$  from below, in approximation B in all cases studied so far the convergence was from above [at least for  $l$  larger than a critical value  $l_{crit}$ —see Eq. (4.2) and Appendix A] such that this scheme behaves as if it did satisfy the upper bound property of the Hylleraas functional.

The Hylleraas functional for the second-order energy is given in (I.7.1–5) in the spin-orbital formalism (equation

numbers with I in front always refer to paper I of the series<sup>4</sup>) and the minimum conditions in (I.7.6,7). The corresponding equations in the spinfree formalism are (I.7.8–11). In the atomic case we go one step further; i.e., we classify doubly excited configurations in terms of the total angular momentum  $L$  of the respective pair. We consider only closed-shell states, and we refer to canonical orbitals.

Let us define symmetry-adapted spinfree two-electron basis functions

$$\begin{aligned} \phi_{SLM}^{PQ} &= [2(1 + \delta_{n_p n_q} \delta_{l_p l_q})]^{-1/2} (-1)^{l_p - l_q + M} \\ &\times (2L + 1)^{1/2} \sum_{m_p m_q} \begin{pmatrix} l_p & l_q & L \\ m_p & m_q & -M \end{pmatrix} \\ &\times \{ \varphi_{n_p l_p m_p}(1) \varphi_{n_q l_q m_q}(2) \\ &+ (-1)^S \varphi_{n_q l_q m_q}(1) \varphi_{n_p l_p m_p}(2) \}. \end{aligned} \quad (2.8)$$

We then expand the symmetry-adapted spinfree pair functions, analogous to Eq. (2.5) but with  $P$  replaced by  $\tilde{P}$  as

$$\begin{aligned} w_{SLM}^{IJ} &= \frac{1}{2} c_{IJ}^{SLM} \{1 - \tilde{P}(1)\} \{1 - \tilde{P}(2)\} r_{12} \phi_{SLM}^{IJ} \\ &+ \sum_{A < B} d_{LM}^S \begin{pmatrix} I & J \\ A & B \end{pmatrix} \phi_{SLM}^{AB}. \end{aligned} \quad (2.9)$$

The coefficients  $d_{LM}^S(\dots)$ , which are independent of  $M$ , are related to the coefficients  $d_L^S(\dots)$  of normalized doubly excited  $n$ -electron configurations  $\tilde{\phi}_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix}$  in the first-order function  $\psi^{(1)}$  as

$$d_L^S \begin{pmatrix} I & J \\ A & B \end{pmatrix} = [(2L + 1)(2S + 1)]^{1/2} d_{LM}^S \begin{pmatrix} I & J \\ A & B \end{pmatrix}, \quad (2.10a)$$

$$\psi^{(1)} = \sum_{S,L} \sum_{I < J} \sum_{A < B} d_L^S \begin{pmatrix} I & J \\ A & B \end{pmatrix} \phi_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix} + \sum_{S,L} \sum_{I < J} c_{IJ}^{SL} \tilde{\phi}_{IJ}^{SL} \quad (2.10b)$$

$$\tilde{\phi}_{IJ}^{SL} = \frac{1}{2} \sum_{\alpha < \beta} R_L^S \begin{pmatrix} I & J \\ \alpha & \beta \end{pmatrix} \phi_L^S \begin{pmatrix} \alpha & \beta \\ I & J \end{pmatrix} [(2S + 1)(2L + 1)]^{1/2} \quad (2.10c)$$

$$R_L^S \begin{pmatrix} I & J \\ \alpha & \beta \end{pmatrix} = \begin{cases} r_L^S \begin{pmatrix} I & J \\ \alpha & \beta \end{pmatrix} & \text{for } \alpha \notin (A, B) \text{ or } \beta \notin (A, B) \\ 0 & \text{for } \alpha \in (A, B) \text{ and } \beta \in (A, B) \end{cases} \quad (2.10d)$$

$\alpha$  and  $\beta$  stand for basis functions not contained in the given basis and  $r_L^S \begin{pmatrix} I & J \\ A & B \end{pmatrix}$  is defined by Eqs. (2.14) and (2.15)

$$\begin{aligned} \phi_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix} &= \frac{1}{2} (2S + 1)^{-1/2} (2L + 1)^{1/2} [(1 + \delta_{n_A n_B} \delta_{l_A l_B})(1 + \delta_{n_I n_J} \delta_{l_I l_J})]^{-1/2} \\ &\times \sum_{m_p, m_q, m_A, m_B, M} \begin{pmatrix} l_J & l_I & L \\ m_J & m_I & -M \end{pmatrix} \begin{pmatrix} l_A & l_B & L \\ -m_A & -m_B & M \end{pmatrix} \\ &\times \{ E_{n_I l_I m_I, n_J l_J m_J}^{n_A l_A m_A, n_B l_B m_B} + (-1)^S E_{n_I l_I m_I, n_J l_J m_J}^{n_B l_B m_B, n_A l_A m_A} \} \phi, \end{aligned} \quad (2.11)$$

where  $E_{PQ}^{RS}$  is a spinfree double replacement operator (see I Secs. II and VI)

$$E_{PQ}^{RS} = \sum_{n, \zeta} a_{R\eta}^\dagger a_{S\zeta}^\dagger a_{Q\zeta} a_{P\eta} \quad (2.12)$$

and where the spin free orbital  $\varphi_R$  is characterized by the quantum numbers  $n_R, l_R, m_R$ .

As in paper I of this series,  $I, J, K, L, M, \dots$  refer to occupied AOs,  $A, B, C, D, \dots$  to unoccupied, and  $P, Q, R, S$  to arbitrary spinfree orbitals.

Let  $\Omega$  be a totally symmetric two-electron operator with the partial-wave expansion

$$\Omega = \sum_n \Omega_n(r_1, r_2) P_n(\cos \vartheta_{12}) \quad (2.13)$$

The  $\Omega$  in Eqs. (2.8)–(2.10) can, e.g., be

$$g = r_{12}^{-1}: \quad g_n = r_{<}^n / r_{>}^{n+1} \quad (2.14a)$$

$$r = r_{12}: \quad r_n = \frac{1}{2n+3} \frac{r_{<}^{n+2}}{r_{>}^{n+1}} - \frac{1}{2n-1} \frac{r_{<}^n}{r_{>}^{n-1}} \quad (2.14b)$$

Then we need the matrix elements

$$\begin{aligned} \Omega_L^S \begin{pmatrix} P & Q \\ R & T \end{pmatrix} &= \langle \phi_{RT}^{SLM} | \Omega | \phi_{SLM}^{PQ} \rangle \\ &= \sum_k \left[ (-1)^{l_P + l_R + L} \begin{Bmatrix} l_P & l_Q & L \\ l_T & l_R & k \end{Bmatrix} \begin{Bmatrix} l_P & k & l_R \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_Q & k & l_T \\ 0 & 0 & 0 \end{Bmatrix} \Omega_k \begin{pmatrix} P & Q \\ R & T \end{pmatrix} \right. \\ &\quad \times (-1)^{l_Q + l_T + S} \begin{Bmatrix} l_R & l_T & L \\ l_P & l_Q & k \end{Bmatrix} \begin{Bmatrix} l_P & k & l_T \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_Q & k & l_R \\ 0 & 0 & 0 \end{Bmatrix} \Omega_k \begin{pmatrix} Q & P \\ R & T \end{pmatrix} \left. \right] \\ &\quad \times [(2l_P + 1)(2l_Q + 1)(2l_R + 1)(2l_T + 1)]^{1/2} [(1 + \delta_{n_P n_Q} \delta_{l_P l_Q})(1 + \delta_{n_R n_T} \delta_{l_R l_T})]^{-1/2} \end{aligned} \quad (2.15a)$$

$$\Omega_k \begin{pmatrix} A & B \\ I & J \end{pmatrix} = \int R_{n_I l_I}^*(r_1) R_{n_J l_J}^*(r_2) \Omega_k(r_1, r_2) R_{n_A l_A}(r_1) R_{n_B l_B}(r_2) r_1^2 dr_1 r_2^2 dr_2. \quad (2.15b)$$

For the operator

$$U = U_{12} = -\frac{1}{2} \frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2) \quad (2.16)$$

the evaluation of the matrix elements is a little more complicated. Details are given in the Appendix C. In terms of STOs closed expressions can be derived for all matrix elements needed in atomic calculations.

The Hylleraas functional for the second-order MP energy becomes

$$F = F_1 + F_2 \quad (2.17)$$

$$F_1 = \sum_{I < J} \sum_{A < B} \sum_{S, L} \left\{ \left| d_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix} \right|^2 (\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J)^{-1} + [(2L + 1)(2S + 1)]^{1/2} 2 \operatorname{Re} d_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix} g_L^S \begin{pmatrix} I & J \\ A & B \end{pmatrix} \right\}. \quad (2.18a)$$

$$F_2 = \sum_{I < J} \sum_{S, L} (2S + 1)(2L + 1) \{ |c_{IJ}^{SL}|^2 (U_{IJ}^{SL} + Q_{IJ}^{SL} - V_{IJ}^{SL}) + 2 \operatorname{Re} c_{IJ}^{SL} V_{IJ}^{SL} \} \quad (2.18b)$$

with

$$V_{IJ}^{SL} \stackrel{\text{sa}}{=} \frac{1}{2} \left\{ 1 - \sum_{P < Q} g_L^S \begin{pmatrix} P & Q \\ I & J \end{pmatrix} r_L^S \begin{pmatrix} I & J \\ P & Q \end{pmatrix} \right\}, \quad (2.19a)$$

$$U_{IJ}^{SL} \stackrel{\text{sa}}{=} \frac{1}{2} \left\{ \frac{3}{2} - \sum_{P < Q} g_L^S \begin{pmatrix} P & Q \\ I & J \end{pmatrix} u_L^S \begin{pmatrix} I & J \\ P & Q \end{pmatrix} \right\}, \quad (2.19b)$$

$$\begin{aligned} Q_{IJ}^{SL} \stackrel{\text{sa}}{=} & \frac{1}{4} \left\{ \left[ (r^2)_L^S \begin{pmatrix} R & J \\ I & J \end{pmatrix} - \sum_{P < Q} r_L^S \begin{pmatrix} P & Q \\ I & J \end{pmatrix} r_L^S \begin{pmatrix} R & J \\ P & Q \end{pmatrix} \right] K_R^I (1 + \delta_{RJ})^{1/2} \right. \\ & \left. + \left[ (r^2)_L^S \begin{pmatrix} I & R \\ I & J \end{pmatrix} - \sum_{P < Q} r_L^S \begin{pmatrix} P & Q \\ I & J \end{pmatrix} r_L^S \begin{pmatrix} I & R \\ P & Q \end{pmatrix} \right] K_R^J (1 + \delta_{IR})^{1/2} \right\} (1 + \delta_{IJ})^{-1/2} \end{aligned} \quad (2.19c)$$

$$K_R^I = \delta(l_I, l_R) (2l_I + 1) \sum_{N, k} (2l_N + 1) \begin{pmatrix} l_N & k & l_I \\ 0 & 0 & 0 \end{pmatrix}^2 g_k \begin{pmatrix} N & I \\ R & N \end{pmatrix}. \quad (2.19d)$$

<sup>sa</sup>  
= means: in the standard approximation (see I Sec. V).

The coefficients  $d_L^S \begin{pmatrix} A & B \\ I & J \end{pmatrix}$  and  $c_{IJ}^{SL}$  are obtained by minimizing the functional (2.18a) and (2.18b). Ignoring Eq. (2.18) one just gets the conventional MP2 schemes.  $F_2$  represents the  $r_{12}$  correction in the approximation B (see paper I), while approximation A is obtained if  $Q_{IJ}^{SL}$  is neglected.

When one truncates the basis at some  $l$ , the error of approximation A is of  $O(l^{-5})$  and that of approximation B of  $O(l^{-7})$ .

If the basis is large enough such that the  $r_{12}$  term has only to take care of the short-range correlation, the varia-

tionally determined coefficients  $c_{IJ}^{SL}$  should reach their asymptotic value, i.e.,<sup>10</sup>

$$\begin{aligned} c_{IJ}^{0L} &= 1 \text{ for natural parity singlet pairs,} \\ c_{IJ}^{1L} &= 1/2 \text{ for triplet pairs,} \\ c_{IJ}^{2L} &= 1/3 \text{ for unnatural parity singlet pairs.} \end{aligned} \quad (2.20)$$

Comparison of the optimized coefficients with their exact asymptotic values is a good check of the near-completeness of the basis.

The  $3j$  and  $6j$  symbols have been evaluated by means of a new algorithm due to Roothaan.<sup>9</sup>

In order to test basis saturation we have used rather large basis sets. It then turns out to be important to choose the basis sets such that near-linear dependences are avoided. Some guiding principles for the choice of the basis sets are discussed in Appendix B.

Usually we have used one and the same basis for all pairs, only occasionally different special basis sets for critical pairs were taken.

Since the calculations were performed on a CYBER 205, we have vectorized the integral evaluation in a way described previously.<sup>11</sup> Also the transformation from primitive integrals to those over orthogonal linear combinations of STOs was partially vectorized.

### III. RESULTS FOR He AND Be

The results of our calculations on the He ground state are displayed in Table I, together with conventional *partial wave increments* (PWI) from Ref. 12. Our conventional PWI with STOs are rather close to those of Ref. 12. Although our GTO basis cannot compete with the STO basis on conventional MP2 level, the MP2-R12 results from the two basis sets (either both A or both B) agree rather well. This indicates that the MP2-R12 is less demanding with respect to basis saturation for the individual PWI.

The MP2-R12 PWI are obtained in the following way. One first performs an MP2-R12 calculation in a basis of  $s$  AOs only and gets an energy ( $-40.792 mE_h$  in approximation A) that one defines as the  $s$  increment. One then performs a calculation with  $s$  and  $p$  and gets a new energy

( $-37.841 mE_h$ ). The difference between the two numbers ( $-2.951 mE_h$ ) is regarded as the  $p$  increment, and so on. In each of these calculations with a truncated partial wave expansion the coefficients  $c_{IJ}^{SL}$  are determined variationally.

It has been checked that the PWI in MP2-R12/B go as  $\sim (l + \frac{1}{2})^{-8}$  as they should go theoretically (see the appendix of part I). In fact these PWI can be regarded as sums of two contributions, namely (a) as basis set truncation errors of the terms that are formally evaluated by completeness insertions and (b) as "genuine" correlation contributions of a scheme, in which the electron interaction  $r_{12}^{-1}$  is replaced by the residual interaction  $U_{12}$  defined by Eq. (2.16). Both contributions go as  $\sim (l + \frac{1}{2})^{-8}$ .

If one starts from the bare-nuclear (rather than Hartree-Fock) Hamiltonian for He-like ions, as has been done in Ref. 3, the genuine contributions can be evaluated directly. These are (for  $l \geq 2$ ) roughly larger by a factor 2 than the PWI (scheme B) in Table I. This suggests that the two contributions (a) and (b) cancel in part, which additionally speeds up the convergence.

If one assumes that the PWI in the column MP2-R12/B(STO) are individually converged, an extrapolation to  $l = \infty$  is easy and leads to  $-37,364 \pm 0.001 mE_h$ . This estimate is lower by  $5 \mu E_h$  than that from Ref. 12, which looks reasonable. In view of our results the estimate of  $-37.372 mE_h$  from Ref. 13 is not easy to explain, because it lies  $8 \mu E_h$  below our probably rather accurate estimate. Either in Ref. 13 unjustified approximations are made or—what seems more likely—our individual PWI have not sufficiently converged. Anyhow an accuracy of  $\sim 10 \mu E_h$  is achieved with  $l \leq 3$  in approximation B.

With approximation A the convergence is not as fast as with approximation B (the increments go  $\sim [l + \frac{1}{2}]^{-6}$ ) but significantly better than in conventional calculations. With MP2-R12/A one overshoots the MP2 correlation energy somewhat if one truncates at small  $l$ , i.e., one approaches  $E^{(2)}$  from below.

The results of the analogous calculations of the Be ground state are collected in Table II. The pattern is similar to that of Table I. Again the convergence is fastest for MP2-R12/B. The STO calculations on this level can be safely ex-

TABLE I. Partial-wave increments to the MP2 energy of the He ground state, negative in millihartree.<sup>a</sup>

$l$	MP2 Ref. 12	MP2 STO	MP2 GTO	MP2-R12/A STO	MP2-R12/A GTO	MP2-R12/B STO	MP2-R12/B GTO
0	13.497	13.496	13.495	40.792	40.791	32.504	32.503
1	18.978	18.974	18.973	-2.951	-2.950	4.598	4.597
2	3.199	3.186	3.129	-0.368	-0.364	0.238	0.240
3	0.931	0.927	0.864	-0.076	-0.077	0.020	0.017
4	0.360	0.355		-0.022		0.002	
$\Sigma_{l,A}^b$	36.965	36.938	36.461	37.375	37.400	37.362	37.357
$\Sigma_{\text{extrap}}$	37.359 <sup>c</sup>			37.364		37.364	

<sup>a</sup>MP2 always means conventional Møller-Plesset second order, MP2-R12 the method presented here, A and B refer to the two variants explained in paper I Secs. V and VII. The basis sets are: STO (12s, 11p, 11d, 9f, 9g), GTO (16s, 10p, 6d, 3f); fully uncontracted basis sets have been used throughout; details on the parameters of the basis sets are given on request.

<sup>b</sup>In the GTO calculations  $\Sigma_{l,3}$ .

<sup>c</sup>With the Gaussian-geminal method  $37.372 mE_h$  were obtained (Ref. 13).

TABLE II. Partial-wave increments to the MP2 pair energies of the Be ground state, negative in millihartrees.<sup>a</sup>

Pair	$l$	MP2 Ref. 12	MP2 STO	MP2 GTO	MP2-R12/A STO	MP2-R12/A GTO	MP2-R12/B STO	MP2-R12/B GTO
$1s^2$	0	12.498	12.485	12.487	40.988	40.989	36.244	36.246
	1	22.477	22.463	22.462	-0.468	-0.472	3.899	3.895
	2	3.549	3.531	3.511	-0.143	-0.142	0.167	0.168
	3	1.005	0.983	0.657	-0.034	-0.007	0.013	0.033
	4	0.382	0.366		-0.009		0.002	
	$\Sigma^b$	39.911	39.828	39.117	40.334	30.368	40.325	40.342
	$\Sigma_{\text{extrap}}$	40.316	(40.340) <sup>c</sup>		40.328		40.326	
$^1S$	0	1.036	1.035	1.035	2.035	2.036	1.815	1.814
	1	1.820	1.819	1.819	1.112	1.110	1.299	1.282
$1s2s$	2	0.265	0.263	0.261	0.095	0.094	0.199	0.101
	3	0.074	0.072	0.052	0.009	0.004	0.014	0.008
	4	0.028	0.027		0.001		0.002	
	$\Sigma^b$	3.223	3.216	3.167	3.252	3.244	3.249	3.205
	$\Sigma_{\text{extrap}}$	3.257	(3.252) <sup>c</sup>		3.250		3.250	
$^3S^d$	0	0.042	0.041	0.041	1.619	1.620	1.281	1.280
	1	1.992	1.993	1.991	0.577	0.576	0.896	0.885
$1s2s$	2	0.150	0.150	0.149	0.021	0.020	0.023	0.033
	3	0.024	0.024	0.020	0.000	-0.002	0.016	0.006
	4	0.006	0.006		0.000		0.001	
	$\Sigma^b$	2.214	2.214	2.201	2.217	2.214	2.217	2.204
	$\Sigma_{\text{extrap}}$	2.220	(2.219) <sup>c</sup>		2.217		2.217	
$2s^2$	0	2.365	2.365	2.362	45.827	45.827	20.071	20.067
	1	22.123	22.123	22.100	-13.347	-13.358	9.821	9.794
	2	3.816	3.812	3.789	-1.539	-1.542	0.554	0.538
	3	1.179	1.175	0.289	-0.291	-0.189	0.065	-0.114
	4	0.472	0.467		-0.080		0.009	
	$\Sigma^b$	29.955	29.942	28.540	30.570	30.738	30.520	30.285
	$\Sigma_{\text{extrap}}$	30.436	(30.536) <sup>c</sup>		30.51		30.523	
	$\Sigma_{\text{tot}}^{(2)b}$	75.303	75.200	72.995	76.373	76.564	76.311	76.036
	$\Sigma_{\text{extrap}}$	76.248	(76.350) <sup>c</sup>		76.32		76.316	

<sup>a</sup> See footnote to Table I; STO basis: 15s, 12p, 11d, 11f, 10g, GTO basis: 20s, 12p, 8d, 3f.

<sup>b</sup> Including  $l = 4$  in STO and  $l = 3$  in GTO calculations.

<sup>c</sup> Best results from the Gaussian geminal method (Ref. 13).

<sup>d</sup> Multiplied by the multiplicity, i.e., sum over all three  $^3S$  pairs.

trapolated to the basis set limit, which gives for the total  $E^{(2)}$ :  $-76.316 mE_h$ .

Like in the case of He our result is lower (by  $32 \mu E_h$ ) than the extrapolation of Jankowski *et al.*<sup>12</sup> from a conventional MP2 calculation, but higher (accidentally by  $32 \mu E_h$ , as well) than the best Gaussian geminal result.<sup>13</sup> For an improved accuracy of our calculations it is certainly not necessary to go beyond  $l = 4$  but one should rather work harder on the basis saturation within the individual  $l$  values.

Again we find that in the MP2-R12/B calculation we approach all pair energies from above. In MP2-R12/A we approach the interorbital correlation energies ( $1s2s$ ,  $^1S$ , and  $^3S$ ) from above, but the intraorbital correlation energies ( $1s^2$  and  $2s^2$ ) from below. In particular one overshoots the correlation energy of the  $2s^2$  pair in an appreciable way in scheme A if one truncates at low  $l$ . While with the STO basis going up to  $l = 4$  the results from approximation A and B differ only by  $0.06 mE_h$ , there is a larger difference between the A and B results obtained with a GTO basis and  $l$  up to 3 ( $0.53 mE_h$ ). In approximation B with GTOs one underestimates the correlation energy of the  $2s^2$  pair in absolute value by about the same amount by which one overestimates it in approximation A.

In comparing the  $1s^2$  and  $2s^2$  pairs we make an interesting observation. The convergence of a conventional PWI is very similar for the two pairs, i.e., the coefficients of the  $(l + \frac{1}{2})^{-4}$  term don't differ very much. This factor is roughly  $150 mE_h$  for the  $1s^2$  and  $210 mE_h$  for the  $2s^2$  pair.<sup>12</sup> The coefficients of the  $(l + \frac{1}{2})^{-8}$  terms, which determine the speed of convergence in the MP2-R12(B) scheme differ, however, much for the two pairs. The ratio of two factors appears to lie between 3 and 5. For the coefficient of the  $(l + \frac{1}{2})^{-6}$  term, which is important for the convergence of MP2-R12(A), there appears to be even a factor of about 10 between the  $2s^2$  and the  $1s^2$  pair.

The gain in the speed of convergence in going from conventional MP2 to MP2-R12 is hence more spectacular for the  $1s^2$  pair than for the  $2s^2$  pair.

Table III gives the values of the coefficients  $c_{II}^{SL}$  of the  $r_{12}$  term as they result from a minimization of the Hylleraas functional. If the basis is large enough that the  $r_{12}$  factor has to take care only of the asymptotic behavior for large  $l$ , the theoretical value of  $c_{II}^{SL}$  should take the values (2.20), which it approaches rather nicely (somewhat faster in scheme A than in scheme B). Convergence to the known asymptotic values is a good check of the basis saturation. The rather

TABLE III. Variationally determined coefficients  $c_{IJ}^{SL}$  of terms linear in  $r_{12}$  for partial-wave expansions up to a given  $l$  for the He and Be ground states.

Pair	$l$	MP2-R12/A	MP2-R12/A	MP2-R12/B	MP2-R12/B
		STO	GTO	STO	GTO
He	0	0.45	0.45	0.32	0.32
$1s^2$	1	0.78	0.78	0.67	0.67
	2	0.89	0.89	0.82	0.82
	3	0.93	0.93	0.89	0.89
	4	0.96		0.93	
	$\infty$	1.0	1.0	1.0	1.0
Be	0	0.46	0.46	0.39	0.39
$1s^2$	1	0.79	0.79	0.73	0.73
	2	0.89	0.89	0.86	0.86
	3	0.94	0.93	0.92	0.92
	4	0.97		0.95	
	$\infty$	1.0	1.0	1.0	1.0
$1s2s$	0	0.09	0.09	0.07	0.07
$^1S$	1	0.41	0.41	0.36	0.34
	2	0.69	0.69	0.64	0.45
	3	0.84	0.83	0.78	0.39
	4	0.90		0.84	
	$\infty$	1.0	1.0	1.0	1.0
$1s2s$	0	0.07	0.07	0.05	0.05
$^3S$	1	0.20	0.20	0.18	0.16
	2	0.31	0.31	0.28	0.15
	3	0.38	0.32	0.32	0.08
	4	0.43		0.29	
	$\infty$	0.5	0.5	0.50	0.5
$2s^2$	0	0.57	0.57	0.23	0.23
	1	0.85	0.85	0.58	0.57
	2	0.92	0.92	0.75	0.74
	3	0.95	0.91	0.84	0.72
	4	0.97		0.89	
	$\infty$	1.0	1.0	1.0	1.0

slow convergence for the  $2s^2$  pair correlates with the slow convergence of the partial wave increments. The relatively poor convergence of  $c_{IJ}^{SL}$  for the interorbital pairs, especially the triplet pair, should not be taken too seriously. Here the

energy improvement due to the  $r_{12}$  term is rather small and the coefficient  $c_{IJ}$  is calculated as a quotient of two numbers which are very small.

#### IV. THE Ne ATOM

The MP2 pair energies of Ne from various calculations are compared in Table IV and the partial wave increments (PWI) from our STO calculations with approximation A and B are displayed in Table V. Let us first have a look at Table V.

The extrapolation to  $l = \infty$  with an error of less than  $0.01 mE_h$  is straightforward and agrees between scheme A and B for all pairs. More difficult is the extrapolation to complete basis sets for the individual PWI. This has been checked by calculations with basis sets of different size. A good test of the basis unsaturation is the accuracy with which one obtains the conventional PWI (see appendix A) although our MP2-R12 PWI converge usually much faster than the conventional ones.

In the column "recommended" in Table IV we have given values based on the ( $l \rightarrow \infty$ ) extrapolations in Table V and estimates of the errors of individual PWI. One notes, e.g., that the ( $l \rightarrow \infty$ ) extrapolation in Table V for the  $2p^2(^3P)$  pair is  $-87.32 mE_h$ , while the conventional result of Ref. 14 is  $-87.35 mE_h$ . Our extrapolated value is (due to incompleteness of the basis for low  $l$ ) hence too high by at least  $0.03 mE_h$ .

Note that in Ref. 14 different basis sets with optimized nonlinear parameters were used for different pairs, while we used essentially the same basis for all pairs. This reduces the flexibility but is advantageous in view of third order and more sophisticated calculations.

Let us look now somewhat more closely at our PWI.

For the  $1s^2$ ,  $1s2s$  and  $2s^2$  pairs the pattern is similar to Table II, with the main difference that there is a change of sign in the PWI of the  $1s^2$  pair in MP2-R12/A. For the  $2p^2$  singlet pairs one finds very large (in absolute value) incre-

TABLE IV. MP2 pair energies for the ground state of the Ne atom negative, in millihartree.

Pair <sup>a</sup>		PW <sup>b</sup>	GG <sup>c</sup>	CBS <sup>d</sup>	MP2-R12/A	MP2-R12/A	MP2-R12/B	MP2-R12/B	Rec. <sup>e</sup>
					STO <sup>e</sup>	GTO <sup>f</sup>	STO <sup>e</sup>	GTO <sup>f</sup>	
$1s^2$	$^1S$	40.22	40.22	40.40	40.24	40.26	40.24	40.23	40.25
$2s2s$	$^1S$	3.97	3.95	3.98	3.97	3.95	3.97	3.94	3.97
	$^3S$	1.59	1.59	1.62	1.58	1.56	1.58	1.56	1.58
$2s^2$	$^1S$	12.02	12.00	12.06	12.02	12.01	12.02	11.91	12.02
$1s2p$	$^1P$	8.13	8.10	7.74	8.17	7.95	8.16	7.89	8.16
	$^3P$	14.04	13.86	13.86	13.90	13.77	13.89	13.77	13.90
$2s2p$	$^1P$	60.33	59.85	59.79	60.43	60.57	60.32	59.31	60.40
	$^3P$	26.82	26.55	26.37	26.71	26.64	26.70	26.46	26.70
$2p^2$	$^1S$	45.56	45.24	44.20	45.52	45.30	45.47	44.95	45.50
	$^1D$	87.85	86.85	87.20	88.01	89.30	87.88	87.25	87.95
	$^3P$	87.39	87.06	87.84	87.36	87.12	87.32	86.85	87.36
$\Sigma$		387.9	385.3	385.1	387.9	388.5	387.6	384.1	387.8

<sup>a</sup>Summed over the multiplicity.

<sup>b</sup>Extrapolated from a conventional partial wave expansion (Ref. 14).

<sup>c</sup>From the Gaussian-geminal method (Ref. 17).

<sup>d</sup>"Basis completeness extrapolation" (Ref. 16).

<sup>e</sup>STO basis 13s, 11p, 10d, 10f, 9g, 5h.

<sup>f</sup>GTO basis 16s, 10p, 7d, 3f.

<sup>g</sup>Recommended values.

TABLE V. Partial wave increments to the MP2 pair energies of the Ne ground state, negative in millihartree with an STO basis.

Pair	$l\ l'$	MP2 Ref. 12	MP2	MP2-R12 A	MP2-R12 B		
$1s^2$	0 0	12.125	12.097	41.026	38.882		
	1 1	22.490	22.443	-0.794	1.194		
	2 2	3.740	3.671	0.000	0.133		
	3 3	1.042	0.929	+0.008	0.028		
	4 4	0.395	0.332	+0.002	0.006		
	5 5	0.179	0.182	0.000	0.000		
	$\Sigma^a$		40.166	39.599	40.242	40.243	
Extrap.		40.22		40.243	40.243		
$1s2s$	0 0	1.655	1.653	3.302	3.111		
	1 1	1.684	1.679	0.517	0.677		
	$^1S$	2 2	0.422	0.416	0.137	0.159	
		3 3	0.116	0.105	0.015	0.019	
		4 4	0.043	0.038	0.002	0.003	
		5 5	0.020	0.013	0.000	0.001	
		$\Sigma^a$		3.962	3.904	3.973	3.970
Extrap.		3.97		3.973	3.971		
$1s2s$	0 0	0.069	0.069	2.308	2.068		
	1 1	1.245	1.242	-0.762	-0.536		
	$^3S$	2 2	0.219	0.219	0.034	0.045	
		3 3	0.036	0.036	0.002	0.003	
		4 4	0.009	0.009	0.000	0.003	
		5 5	0.003	0.000	0.000	0.000	
		$\Sigma^a$		1.581	1.576	1.582	1.580
Extrap.		1.59		1.582	1.580		
$2s^2$	0 0	3.182	3.182	45.381	26.896		
	1 1	1.843	1.839	-32.491	-15.628		
	$^1S$	2 2	4.623	4.603	-0.651	+0.678	
		3 3	1.303	1.281	-0.154	+0.055	
		4 4	0.504	0.495	-0.043	+0.008	
		5 5	0.233	0.191	-0.019	-0.000	
		$\Sigma^a$		11.947	11.591	12.022	12.009
Extrap.		12.02		12.01	12.01		
$1s2p$	0 1	0.240	0.240	4.448	4.015		
	1 2	6.015	6.012	3.366	3.720		
	$^1P$	2 3	1.215	1.209	0.331	0.386	
		3 4	0.363	0.360	0.029	0.039	
		4 5	0.144	0.129	0.001	0.001	
		$\Sigma^a$		8.070	7.950	8.173	8.161
		Extrap.		8.13		8.17	8.16
$1s2p$	0 1	6.102	6.102	11.390	10.848		
	1 2	7.047	7.047	2.411	2.917		
	$^3P$	2 3	0.603	0.603	0.095	0.124	
		3 4	0.108	0.099	0.001	0.004	
		4 5	0.027	0.018	0.000	0.001	
		$\Sigma^a$		13.896	13.867	13.896	13.892
		Extrap.		14.04		13.90	13.89
$2s2p$	0 1	24.474	24.474	139.141	99.944		
	1 2	12.594	12.549	-76.468	-41.340		
	$^1P$	2 3	14.502	14.412	-1.677	+1.551	
		3 4	4.554	4.485	-0.425	+0.157	
		4 5	1.878	1.674	-0.143	+0.003	



TABLE V. (continued).

Pair	$l l'$	MP2 Ref. 12	MP2	MP2-R12 A	MP2-R12 B
	$\Sigma^a$	59.868	57.591	60.428	60.315
	Extrap.	60.33		60.32	60.32
$2s2p$	0 1	18.144	18.144	62.916	47.352
	1 2	4.581	4.581	- 35.751	- 20.969
$^3P$	2 3	3.141	3.132	- 0.387	+ 0.266
	3 4	0.585	0.567	- 0.059	+ 0.046
	4 5	0.162	0.153	- 0.013	0.000
	$\Sigma^a$	26.685	26.576	26.706	26.695
	Extrap.	26.82		26.695	26.695
$2p^2$	0 0	2.294	2.291	974.731	190.135
	1 1	15.207	15.186	- 928.075	- 151.434
$^1S$	2 2	20.777	20.737	- 0.655	6.291
	3 3	4.300	4.249	- 0.325	0.440
	4 4	1.469	1.450	- 0.095	0.060
	5 5	0.637	0.546	- 0.046	0.006
	6 6	0.321	0.257	- 0.011	0.002
	$\Sigma^a$	45.356	44.460	45.514	45.488
	Extrap.	45.56		45.49	45.49
$2p^2$	0 2	6.695	6.690	7856.782	6902.371
	1 1	40.055	40.035	- 7761.645	- 6829.321
$^1D$	1 3	3.950	3.890	- 8.946	12.882
	2 2	23.255	23.230	+ 2.047	- 0.988
	2 4	4.940	4.900	- 0.203	+ 2.917
	3 3	3.320	3.290	+ 0.136	- 0.368
	3 5	1.860	1.690	- 0.143	+ 0.478
	4 4	0.960	0.950	- 0.002	- 0.121
	4 6	0.850	0.740	- 0.052	+ 0.105
	5 5	0.380	0.330	- 0.015	- 0.044
	6 6	0.180	0.150	- 0.004	+ 0.027
	$\Sigma^a$	87.475	85.904	87.955	87.878
	Extrap.	87.85		87.90	87.89
$2p^2$	1 1	41.238	41.229	93.241	78.864
	2 2	40.365	40.356	- 5.370	8.126
$^3P$	3 3	4.374	4.356	- 0.455	0.300
	4 4	0.918	0.918	- 0.069	0.027
	5 5	0.270	0.270	- 0.020	0.002
	6 6	0.099	0.090	- 0.006	- 0.001
	$\Sigma$	87.345	87.211	87.321	87.315
	Extrap.	87.39		87.32	87.32
$E^{(2)}$		386.35	378.65	387.81	387.55
	Extrap.	387.92		387.60	387.57

<sup>a</sup>Sum up to  $l = 6$  or  $l = 9$  depending on the pair in Ref. 14, up to  $l = 5$  in the present calculations, but up to  $l = 6$  for  $2p^2$  pairs.

ments for the low partial waves ( $ss$ ,  $sd$ ,  $pp$ ). These can be explained in the following way. An ingredient of our method consists in evaluating certain matrix elements by means of completeness insertions. Some of these matrix elements, mainly those of the type

$$\langle \varphi(1,2,3) | r_{12} r_{13}^{-1} | \varphi(1,2,3) \rangle \quad (4.1)$$

have a finite partial wave expansion that breaks off after a fixed  $l$  value. This means that in order to apply a completeness insertion, the basis need only be complete up to this  $l$  value. Functions with higher  $l$  are not required in this context. The critical  $l$  depends on the angular quantum numbers  $l_1$  and  $l_2$  of the pair considered and the maximum  $l$ -value  $l_{\max}$

of occupied AOs (see appendix A)

$$l_{\text{crit}} = l_1 + l_2 + l_{\max}. \quad (4.2)$$

In He or Be we have  $l_{\text{crit}} = 0$ , in Ne for  $nsms$  pairs  $l_{\text{crit}} = 1$  and  $2p^2$  pairs  $l_{\text{crit}} = 3$ .

If one applies either standard approximations to the  $2p^2$  pair of Ne, but uses a basis of  $s$  and  $p$  functions only, one does something unreasonable, and the large values in Table V for  $ss$ ,  $sd$ , and  $pp$ , which nearly cancel, are a sort of an artifact. One should rather not separate them, but add everything up to  $l_{\text{crit}}$ . This sum is 46.637, 95.137 in MP2-R12/A and 38.694, 73.050 in MP2-R12/B, for the  $^1S(2p^2)$  and  $^1D(2p^2)$  pair, respectively. In an actual calculation the individual

contributions never appear, only the partial sums up to a given  $l$ , and these special sums are irrelevant, as long as the basis does not contain  $s, p, d, f$ .

As expected the convergence generally is fastest for MP2-R12/B, but even MP2-R12/A converges much faster than conventional MP2. We generally observe that in MP2-R12/B the PWI are all negative if  $l$  is larger than the critical  $l$  value (see appendix A), i.e., for  $l > 1$  for *nsms* pairs,  $l > 2$  for *nsmp* pairs, and  $l > 3$  for *npm* pairs. This means that for  $l > l_{\text{crit}}$  MP2-R12/B approaches the exact energy from above, like a genuine variational approach. For MP2-R12/A the pair correlation energies of some pairs ( $2s^2, 2s2p, 2p^2$ ) are approached from below, i.e., on truncating at a too low  $l$  one can overshoot the MP2 correlation energy.

Let us now look at Table IV.

The first observation that one makes is that all total MP2 energies reported in this table agree to within  $\sim 1\%$ . (We have not included our conventional MP2 results, but these can, for the STO calculations be seen from Table V.)

If we compare our recommended values with the extrapolations from Ref. 14 we note that compared to our estimates, Jankowski *et al.*<sup>14</sup> systematically overestimate (in absolute value) all triplet pairs and underestimate all singlet pairs, in a way that the total estimates agree to within  $0.1 mE_h$ . Another extrapolation of  $-388.3 mE_h$  has been published by Lindgren *et al.*<sup>15</sup> In comparing the three estimates one should consider that our extrapolation of  $-387.7 mE_h$  is based on a calculated value of  $-387.4 mE_h$  (approximation B), the extrapolation of  $-387.9 mE_h$ <sup>14</sup> on a calculated value (PWI up to  $l = 9$ ) of  $-386.4 mE_h$  and the extrapolation of  $-388.3 mE_h$ <sup>15</sup> on a calculated value (PWI up to  $l = 6$ ) of  $383.6 mE_h$ .

Unfortunately we cannot tell how accurate our recommended value is. Basis saturation tests are rather hard with STOs, mainly due to problems of near linear dependences. One would probably be better off with a numerical basis like that recently proposed by Salomonsen and Öster.<sup>20</sup> Anyway the error of our extrapolation should not be greater than a few tenths of a millihartree.

The Gaussian-geminal (GG) value ( $385.3 mE_h$ ) is the result of a very sophisticated calculation involving as many as 1226 nonlinear variational parameters.<sup>17</sup> The result is less good than in the case of He or Be, probably because the nonlinear parameters are still far from optimal.<sup>18</sup>

In Table IV one also finds the results of the “complete-basis set extrapolation” by Petersson *et al.*<sup>16</sup> This does not claim to be very accurate, but it is astonishingly good for its simplicity and it is also applicable to more complicated systems.

A conventional relativistic and nonrelativistic MP2 calculation with rather large GTO basis sets, the largest one being  $14s, 10p, 8d, 6f, 5g, 4h$  (yielding  $E_2 = 378.07 mE_h$  and a relativistic correction of  $0.23 mE_h$ ) has recently been published.<sup>19</sup> The best MP2 energy of Ref. 19 differs from the basis set limit by almost 3%.

## V. Mg, Ar, AND Ca

In Table VI the MP2 pair energies of the Mg atom are collected.

The pattern is, of course, similar to that for Ne. Our recommended values agree on the whole rather well with the extrapolations of Jankowski *et al.*<sup>21</sup> The unbalance between the extrapolation for singlet and triplet pairs observed in the case of Ne<sup>14</sup> is not duplicated. The differences between our results and those of Ref. 21 are generally a few hundreds of a millihartree. Somewhat larger differences 0.2 to 0.3  $mE_h$  are found for the  $1s2p(^1P)$ ,  $2s2p(^1P)$  and  $2p^2(^1D)$  pairs. An unexpected large difference ( $2.5 mE_h$ ) arises for the MP2 energy of the  $3s^2$  pair.

We have therefore analyzed this pair in more detail (see Table VII) and found that there is already a difference in the conventional MP2 calculations in the  $pp$  increment of 2.4  $mE_h$ , which accounts exactly for the difference between our and Jankowski's results. We can only conclude that there was a misprint or rather a copy error in Ref. 21. (The sum of all pairs cf. Ref. 21 is consistent with the “wrong” value in the table.) A further hint that the pair energy of 27.74  $mE_h$  for the  $3s^2$  pair of Ref. 21 is probably incorrect was found in the following way. Fortunately Jankowski *et al.* have also published the partial wave increment for the isoelectronic ions Na<sup>-</sup>, Si<sup>2+</sup>, Ar<sup>8+</sup>, and Zn<sup>18+</sup>.<sup>22</sup> The value for the  $l = 2$  increment of the  $3s^2$  pair published in Ref. 21 does not fit into a smooth curve through the other values, while our result does. The MP2 extrapolation for the total correlation energy of Ref. 21 must hence be corrected to 425.5  $mE_h$ . This can be compared to our recommended value of 426.7  $mE_h$ , which we regard as accurate to within a few tenths of a millihartree.

The calculations for Table VII were done with a basis different from that for Table VI. Therefore the figures don't agree exactly.

The results for argon (Table VIII) fit into the general trend. The results from approximations A and B (in the STO basis) differ a little more than for the smaller systems, but still by less than 0.5% of the correlation energy. To reduce this difference and to estimate a reliable recommended value would require larger basis sets (which would cause numerical instability problems with our method). The extrapolated value from the Jankowski group<sup>21</sup> of 706.00  $mE_h$  lies between our A and B results and can probably be regarded as a recommended value.

In the GTO calculations the results from approximation A and B differ somewhat more (by  $\sim 2\%$ ). This is the only case observed by us so far, where MP2-R12/A calculations with a rather good GTO basis underestimate the basis set limit of MP2 (see Table XV and Sec. VII).

Ar is the first example of an atom where pair functions with unnatural parity ( $^1P, ^3S$ , and  $^3D$  to the configuration  $2p3p$ ) are present. It has been shown<sup>10</sup> that for such states even the conventional partial-wave increments go as  $l^{-8}$ , such that with MP2-R12 one can hardly improve anything. One sees from Table VIII that for these states the switch from conventional MP2 to MP2-R12/A or B has almost no effect (usually less than 0.01  $mE_h$ ). Since the  $r_{12}$  correction matters so little, it has not been possible to check numerically that the coefficient  $c_{12}$  reaches asymptotically the value  $1/3$  (2.20) predicted theoretically.<sup>10</sup>

If we take the  $^1P(2p3p)$  as an example of an unnatural

TABLE VI. MP2 pair energies for the ground state of the Mg atom, negative in millihartree.

Pair <sup>a</sup>		MP2 STO <sup>d</sup>	MP2 <sup>b</sup> Extrap.	MP2-R12/A STO <sup>d</sup>	MP2-R12/A GTO <sup>e</sup>	MP2-R12/B STO <sup>d</sup>	MP2-R12/B GTO <sup>e</sup>	MP2 GTO <sup>e</sup>	Rec. <sup>c</sup>
1s <sup>2</sup>	<sup>1</sup> S	38.55	39.66	39.50	39.57	39.49	39.53	36.65	39.62
1s2s	<sup>1</sup> S	4.27	4.41	4.38	4.37	4.38	4.36	4.06	4.38
	<sup>3</sup> S	1.54	1.55	1.55	1.54	1.55	1.54	1.49	1.55
2s <sup>2</sup>	<sup>1</sup> S	11.15	11.58	11.60	11.62	11.59	11.55	10.29	11.60
1s2p	<sup>1</sup> P	9.84	9.90	10.14	10.09	10.14	10.03	8.16	10.14
	<sup>3</sup> P	16.73	16.74	16.79	16.75	16.78	16.73	16.23	16.79
2s2p	<sup>1</sup> P	51.45	55.62	56.36	56.74	56.27	55.97	46.00	56.35
	<sup>3</sup> P	23.37	23.67	23.66	23.69	23.66	23.60	22.65	23.66
2p <sup>2</sup>	<sup>1</sup> S	45.48	46.57	46.62	46.58	46.59	46.40	43.05	46.60
	<sup>1</sup> D	83.75	86.60	86.97	87.47	86.87	86.39	74.02	86.95
	<sup>3</sup> P	85.21	85.41	85.43	85.40	85.42	85.27	83.64	85.44
1s3s	<sup>1</sup> S	0.17	0.18	0.18	0.17	0.17	0.16	0.16	0.17
	<sup>3</sup> S	0.08	0.09	0.09	0.08	0.08	0.08	0.08	0.08
2s3s	<sup>1</sup> S	0.90	0.93	0.91	0.90	0.91	0.85	0.83	0.91
	<sup>3</sup> S	0.77	0.78	0.77	0.76	0.77	0.73	0.73	0.77
2p3s	<sup>1</sup> P	5.86	5.94	5.93	5.91	5.88	5.61	5.33	5.92
	<sup>3</sup> P	10.59	10.62	10.59	10.59	10.59	10.44	10.36	10.59
3s <sup>2</sup>	<sup>1</sup> S	24.36	27.74 <sup>f</sup>	25.19	25.79	24.95	25.05	22.91	25.20
Σ		414.07	427.99 <sup>g</sup>	426.7	428.0	426.1	424.3	386.6	426.7

<sup>a</sup> Summed over the multiplicity.<sup>b</sup> Extrapolated from a conventional partial wave expansion (Ref. 21).<sup>c</sup> Recommended values.<sup>d</sup> STO basis: 12s, 12p, 10d, 9f, 8g, 5h.<sup>e</sup> GTO basis: 17s, 13p, 7d, 3f.<sup>f</sup> This value is probably incorrect, see Table VII and the discussion in Sec. V.<sup>g</sup> With the 3s<sup>2</sup> increment corrected the sum becomes 425.5.

parity singlet pair, we see that with  $l$  up to 5 all three calculations (conventional MP2, MP2-R12/A, and MP2-R12/B) converge to a pair increment of  $1.604 mE_h$ . The truncation error at  $l = 2$  is  $0.102 mE_h$  in MP2<sub>conv</sub>,  $0.012 mE_h$  in MP2-R12/A, and  $0.023 mE_h$  in MP2-R12/B.

It should be pointed out (this is not limited to Ar) that no special care is needed for the correlation energy of the inner shells, and for the interaction of inner shells with valence shells. In conventional calculations “steep” polarization functions are needed, which blow up the basis. Calculations of the valence-shell correlation energy only are then much cheaper. Such steep polarization functions are not required in the MP2-R12 method, the core correlation energy is therefore nearly “free of extra charge.”

In the case of Ar we can also compare with a recent conventional MP2 with a large GTO basis.<sup>23</sup> Wells and Wilson<sup>23</sup> used a much larger basis [22s, 20p, 13d, 5f] than we did [17s, 13p, 7d, 2f], in our GTO calculations but they got a

smaller (in absolute value) conventional MP2-correlation energy ( $-598.1 mE_h$ , compared to our *conventional* result  $-604.8 mE_h$ ). We have not included the result of Ref. 23 in Table VIII, because in Ref. 23 only the sums of singlet and triplet contributions are tabulated. A detailed comparison reveals that Wells and Wilson<sup>23</sup> got somewhat better pair energies for the core contributions, but poorer energies of valence pairs. Though there is nothing to object to this calculation, we must refute a conclusion made in Ref. 23, namely that the extrapolations of Jankowski *et al.*<sup>21</sup> need to be revised. In comparing their results with those of Ref. 21, Wells and Wilson failed to include the increments with  $l \neq l'$  (e.g., *sd*) evaluated by Jankowski *et al.* So they came to the erroneous conclusion that Jankowski *et al.* miss some  $14 mE_h$  and that the extrapolated MP2 energies should be changed from 706 to 722  $mE_h$ .

Ca is the last closed-shell atom with only occupied *s* and *p* AOs. The MP2 pair correlation energies are listed in Table IX. In this case the basis-set limit extrapolations by Jankowski *et al.* were only published<sup>22</sup> after our first calculations had been performed<sup>24</sup> and we were pleased with the good agreement. The difference between approximations A and B is only  $\sim 1 mE_h$  for the STO calculations and  $\sim 10 mE_h$  for GTOs. The extrapolated value of 798.3 from Jankowski *et al.*<sup>22</sup> lies between our A and B (STO) results and it can be taken as recommended value.

In Table X results from various different GTO basis sets and two STO basis sets for Ca are collected. This table is meant as a warning that the MP2-R12 method is far from being foolproof. None of the GTO basis sets in Table X is really small from a conventional point of view. They all contain several *d* functions and one *f* function, but even conventionally their different quality is obvious, as is seen from the SCF energies (variations of more than  $300 mE_h$ ) and the

TABLE VII. Partial-wave increments (negative in millihartree) for the 3s<sup>2</sup> pair of the Mg ground state.

$l$	MP2 STO	MP2 GTO	MP2 STO	MP2-R12/A STO
	This work	This work	Ref. 21	This work
0	1.58	1.58	1.59	49.22
1	17.52	17.51	19.92	-21.46
2	3.92		3.93	-1.92
3	1.22		1.23	-0.37
4	0.35		0.50	-0.13
Σ( $l < 4$ )	24.59		27.17	25.34
Σ( $l < \infty$ )	25.2		27.74	25.2

Basis set STO: 12s, 11p, 11d, 11f, 7g; GTO: 28s, 24p.

TABLE VIII. MP2 pair energies for the ground state of the Ar atom, negative in millihartree.

Pair		MP2 STO	MP2 Extrap. <sup>a</sup>	MP2-R12/A STO	MP2-R12/A GTO	MP2-R12/B STO	MP2-R12/B GTO	MP2 GTO
1s <sup>2</sup>	<sup>1</sup> S	35.50	37.82	37.99	37.85	37.98	37.80	33.64
1s2s	<sup>1</sup> S	4.84	5.17	5.15	5.10	5.15	5.10	4.59
	<sup>3</sup> S	1.43	1.47	1.46	1.45	1.46	1.45	1.36
2s <sup>2</sup>	<sup>1</sup> S	11.04	11.48	11.53	11.43	11.52	11.37	9.95
1s2p	<sup>1</sup> P	12.22	12.99	13.28	13.03	13.27	12.96	9.49
	<sup>3</sup> P	20.49	20.61	20.69	20.64	20.69	20.62	19.55
2s2p	<sup>1</sup> P	46.55	49.77	49.90	49.61	49.84	48.94	36.35
	<sup>3</sup> P	20.85	20.97	21.01	20.87	21.00	20.78	19.35
2p <sup>2</sup>	<sup>1</sup> S	45.52	46.75	46.88	46.45	46.86	46.29	41.78
	<sup>1</sup> D	78.59	81.55	82.41	83.91	82.37	82.90	65.44
	<sup>3</sup> P	79.81	80.10	80.10	79.76	80.10	79.63	77.01
1s3s	<sup>1</sup> S	0.49	0.52	0.49	0.51	0.49	0.47	0.47
	<sup>3</sup> S	0.19	0.18	0.23	0.19	0.19	0.18	0.18
1s3p	<sup>1</sup> P	0.86	0.90	0.88	0.73	0.87	0.72	0.67
	<sup>3</sup> P	1.42	1.44	1.42	1.36	1.42	1.36	1.35
2s3s	<sup>1</sup> S	2.05	2.12	2.14	2.13	2.06	2.01	1.73
	<sup>3</sup> S	1.26	1.29	1.30	1.26	1.26	1.20	1.12
2p3s	<sup>1</sup> P	7.38	7.29	7.71	7.50	7.43	7.15	5.95
	<sup>3</sup> P	9.27	9.27	9.41	9.23	9.28	9.02	8.48
2s3p	<sup>1</sup> P	3.84	3.81	3.93	3.56	3.90	3.41	2.70
	<sup>3</sup> P	5.44	5.40	5.45	5.13	5.44	5.02	4.59
2p3p	<sup>1</sup> S	6.13	6.29	6.17		6.15		
	<sup>1</sup> P	1.60	1.62	1.61		1.61		
	<sup>1</sup> D	14.59	15.00	14.86		14.79		
	<sup>1</sup> S + <sup>1</sup> P + <sup>1</sup> D	22.32	22.91	22.64	22.36	22.55	21.88	19.14
	<sup>3</sup> S	4.12	4.14	4.13		4.13		
	<sup>3</sup> P	16.15	16.20	16.16		16.16		
	<sup>3</sup> D	8.53	8.55	8.55		8.54		
	<sup>3</sup> S + <sup>3</sup> P + <sup>3</sup> D	28.81	28.89	28.84	28.42	28.82	28.12	26.59
3s <sup>2</sup>	<sup>1</sup> S	10.48	10.93	10.97	11.04	10.72	10.72	9.21
3s3p	<sup>1</sup> P	45.42	48.00	48.63	48.59	48.04	45.39	35.03
	<sup>3</sup> P	15.00	15.12	15.13	14.78	15.04	14.28	13.70
3p <sup>2</sup>	<sup>1</sup> S	41.84	43.06	43.05	42.06	42.67	41.02	38.26
	<sup>1</sup> D	63.55	66.85	66.68	67.74	66.69	61.45	50.61
	<sup>3</sup> P	68.97	69.30	69.12	68.15	69.07	67.54	66.50
Σ		685.4	706.0	708.4	704.9	706.2	688.8	604.8

<sup>a</sup>Reference 21; Basis set STO: 12s, 12p, 12d, 11f, 10g, 5h; Basis set GTO: 17s, 13p, 7d, 2f.

conventional MP2 energies (ranging between 51.9% and 80% of the estimated limit). The variations in the MP2-R12 energy are smaller but far from negligible. The worst case is basis B which yields 123.2% of the MP2-R12 energy compared to 51.9% on conventional MP2 level. While basis sets C, D, and E have to be regarded as acceptable for an MP2-R12 calculation and basis E as quite good, basis sets A and B are inadequate. If one analyzes the pair contributions, one sees that most pairs are rather well-described by all basis sets, but there are a few "critical" pairs. Basis A is entirely incapable of describing any pair that involves a 4s AO, but is otherwise not too bad. Basis B has serious difficulties with pairs that involve a 2p AO. In all these cases the pair energies are considerably overestimated, mainly because the basis is unable to satisfy the required completeness relations.

It is easily seen what is wrong with these basis sets. In basis A the smallest exponent of *p* AOs is  $\eta = 0.34$ , while  $\eta = 0.07$  is required as partner of the *s* AOs with  $\eta = 0.04$ , that dominates in the 4s AO (see appendix B). Therefore all pairs involving 4s are incorrect—but so in a more drastic way than in a conventional calculation. Basis B does contain

a *p* basis function with  $\eta = 0.05$ , but it lacks *d*-type basis functions with  $\eta \approx 10$  that are needed as partner for the 2p AO.

The two STO basis sets G and H differ mainly in the maximum *l* included, namely  $l = 4$  for basis G and  $l = 5$  for basis H. For conventional MP2 there is a substantial difference. One gets  $\sim 94\%$  of the basis set limit for basis G, 96% for basis H. On MP2-R12/A level there is hardly a difference between the two basis sets.

## VI. Cu<sup>+</sup>, Zn<sup>2+</sup>, Zn, and Kr

The next closed-shell configuration after that of Ca is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  which is realized for an excited state of Ni and for the ground states of Cu<sup>+</sup> and Zn<sup>2+</sup>. We have chosen the latter two and especially Zn<sup>2+</sup> due its relation to neutral Zn, which has also a closed-shell ground state with an additional 4s<sup>2</sup> occupation.

The results for Zn<sup>2+</sup> and Zn are collected in Table XI, those for Cu<sup>+</sup> in Table XIII, while in Table XII the partial wave increments (PWI) of the 3d<sup>2</sup> pairs of Zn are studied in more detail.

TABLE IX. MP2 pair energies for the ground state of the Ca atom, negative in millihartree.

Pair		MP2 STO	MP2 Extrap. <sup>a</sup>	MP2-R12/A STO	MP2-R12/A GTO	MP2-R12/B STO	MP2-R12/B GTO	MP2 GTO
1s <sup>2</sup>	<sup>1</sup> S	33.56	37.28	37.73	37.39	37.69	37.35	33.25
1s2s	<sup>1</sup> S	4.76	5.28	5.40	5.25	5.39	5.25	4.72
	<sup>3</sup> S	1.35	1.44	1.62	1.43	1.62	1.43	1.34
1s3s	<sup>1</sup> S	0.58	0.63	0.64	0.64	0.64	0.63	0.58
	<sup>3</sup> S	0.21	0.24	0.22	0.22	0.22	0.22	0.21
1s4s	<sup>1</sup> S	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	<sup>3</sup> S	0.01	0.01	0.01	0.01	0.01	0.01	0.01
2s <sup>2</sup>	<sup>1</sup> S	10.91	11.45	11.45	11.38	11.44	11.33	9.87
2s3s	<sup>1</sup> S	2.38	2.49	2.49	2.50	2.49	2.46	1.99
	<sup>3</sup> S	1.40	1.41	1.43	1.41	1.43	1.40	1.29
2s4s	<sup>1</sup> S	0.14	0.15	0.14	0.13	0.14	0.12	0.12
	<sup>3</sup> S	0.10	0.10	0.10	0.09	0.10	0.09	0.09
3s <sup>2</sup>	<sup>1</sup> S	10.64	11.11	11.14	11.27	11.11	11.04	9.09
3s4s	<sup>1</sup> S	1.17	1.22	1.21	1.15	1.19	1.07	0.92
	<sup>3</sup> S	0.87	0.90	0.87	0.85	0.87	0.81	0.76
4s <sup>2</sup>	<sup>1</sup> S	20.92	22.22	21.72	22.36	21.52	20.58	18.55
1s2p	<sup>1</sup> P	12.39	13.71	13.94	13.56	13.94	13.48	9.78
	<sup>3</sup> P	20.75	21.24	21.18	21.18	21.18	21.16	20.01
1s3p	<sup>1</sup> P	1.17	1.26	1.32	1.23	1.32	1.19	0.92
	<sup>3</sup> P	1.92	1.98	1.96	1.93	1.96	1.92	1.85
2s2p	<sup>1</sup> P	44.65	48.12	48.49	48.28	48.43	47.70	34.73
	<sup>3</sup> P	20.18	20.52	20.42	20.31	20.42	20.23	18.71
2s3p	<sup>1</sup> P	4.92	5.22	5.24	5.12	5.24	4.94	3.28
	<sup>3</sup> P	7.00	7.11	7.08	7.12	7.08	6.98	5.76
3s2p	<sup>1</sup> P	7.81	8.19	8.21	8.06	8.20	7.89	6.15
	<sup>3</sup> P	9.21	9.36	9.28	9.18	9.27	9.10	8.39
3s3p	<sup>1</sup> P	45.16	48.57	48.78	49.75	48.58	47.40	32.23
	<sup>3</sup> P	13.07	13.23	13.22	13.25	13.21	12.96	11.50
4s2p	<sup>1</sup> P	0.60	0.66	0.61	0.54	0.61	0.52	0.51
	<sup>3</sup> P	0.91	0.90	0.91	0.88	0.91	0.87	0.87
4s3p	<sup>1</sup> P	10.32	10.56	10.55	10.41	10.49	9.89	8.75
	<sup>3</sup> P	19.14	19.26	19.21	19.11	19.19	18.90	18.49
2p <sup>2</sup>	<sup>1</sup> S	45.14	46.67	46.73	46.37	46.75	46.24	41.52
	<sup>1</sup> D	76.66	81.05	81.06	83.05	81.10	82.15	63.69
	<sup>3</sup> P	78.68	79.29	79.03	78.76	79.04	78.64	75.77
2p3p	<sup>1</sup> S + <sup>1</sup> P + <sup>1</sup> D	28.35	29.27	29.20	30.38	29.04	29.80	24.19
	<sup>3</sup> S + <sup>3</sup> P + <sup>3</sup> D	35.97	36.33	36.16	36.83	36.12	36.45	33.08
3p <sup>2</sup>	<sup>1</sup> S	47.43	48.82	48.89	48.90	48.77	48.28	43.07
	<sup>1</sup> D	69.06	73.05	73.19	76.56	72.84	73.06	54.31
	<sup>3</sup> P	77.62	77.94	77.92	77.85	77.88	77.39	74.61
Σ		767.1	798.3	798.8	804.7	797.5	791.0	674.9

<sup>a</sup> Reference 22. STO basis: 15s, 13p, 12d, 11f; 10g, 5h; GTO basis: 20s, 15p, 8d, 2f.

Now the critical  $l$  value  $l_{\text{crit}}$  needed to satisfy the completeness relation for integrals of the type (4.1) is by virtue of (4.2)  $l_{\text{crit}} = 6$ , at least for  $d^2$  pairs ( $l = 5$  for  $pd$  pairs). In the atomic program it has been possible to include  $l = 6$  ( $i$  functions), while with the molecular program we could not go beyond  $l = 3$ .

One sees from Table XII that the PWI of MP2-R12/A have no direct physical meaning as long as  $l < l_{\text{crit}}$  (like has been seen in Table V for  $2p^2$  pairs) and that one would get absurd results if one truncates at  $l = 1(p)$  or  $l = 2(d)$ . However, it appears that the PWI decrease (in absolute value; though not monotonically) with  $l$  to the extent that truncation at  $l = 4(g)$  causes errors of the order of a fraction of a  $mE_h$  and truncation at  $l = 3(f)$  errors of the order of some  $10 mE_h$  (actually an overestimation of the pair correlation energy).

Table XI gives the MP2-R12 pair contribution for

$\text{Zn}^{2+}$  and Zn from calculations with the atomic and the molecular program, compared with extrapolated basis set limits.<sup>25</sup> On the whole the agreement is as good as for the lighter atoms. Only for the pairs  $2p^2$  and  $2p3p$  there are differences of a few millihartrees, but for the total second-order energy differences of less than  $10 mE_h \approx 0.6\%$  are found which is quite consistent with the results from Sec. IV. We are not able to explain the discrepancies for the  $2p^2$  and  $2p3p$  pairs—even at conventional MP2 level. The fact that we had started with an SCF calculation in the full basis, while Janowski *et al.*<sup>25</sup> used a rather small basis for the SCF calculations and different large ones for the various pair correlations, appears to account only for a part of this discrepancy.

The results for the isoelectronic  $\text{Cu}^+$  are documented in Table XII. Here reference values are available only for some selected pairs.<sup>26</sup>

We have also included the results for the  $\text{Cu}^+$  "core" in

TABLE X. Results of MP2-R12/A calculations on the Ca ground state with different basis sets,<sup>a</sup> energies negative in millihartree.

	A	B	C	D	E	F	G	H
Basis	8,6,3,1	10,8,3,1	15,9,4,1	16,13,5,1	16,13,6,2	20,15,8,2	STO	STO
$E_{\text{SCF}} - 676E_h$	404.18	409.91	667.07	745.53	746.16	757.37	758.07	758.17
MP2 $\Sigma$	490.2	414.9	585.8	596.1	638.8	674.9	749.7	766.5
MP2 in % of 798.3	61.4	51.9	73.3	74.6	80.0	84.5	93.9	96.0
MP2-R12								
$ns^2; n < 4$	59.41	60.04	59.00	59.59	59.55	60.04	60.22	60.32
$4s^2$	53.80	23.03	20.66	21.44	22.66	22.36	21.90	21.72
$nsn's; n \neq n' < 4$	12.14	11.74	10.22	10.77	10.97	11.47	11.44	11.80
$4sn's; n' < 4$	15.89	1.97	1.78	2.03	2.35	2.26	2.37	2.36
$nsn'p; n < 4; n' \neq n$	65.73	71.74	62.04	64.40	65.84	67.39	67.86	68.21
$4sn'p;$	64.66	27.54	28.62	29.33	30.87	30.93	31.56	31.28
$2s2p$	76.25	164.47	69.90	70.37	70.17	68.58	68.75	68.91
$3s3p$	54.51	52.65	63.69	62.82	62.16	63.00	61.77	62.00
$2p^2$	227.70	329.65	218.78	220.33	212.98	208.18	206.61	206.82
$2p3p$	57.18	57.01	61.36	60.81	61.95	67.12	65.49	65.36
$3p^2$	190.16	189.10	220.59	217.06	203.21	203.31	199.72	200.00
MP2-R12 $\Sigma$	877.4	988.9	816.6	819.0	802.7	804.7	797.6	798.8
MP2 in % of 798.3	109.9	123.9	102.3	102.6	100.6	100.8	99.9	100.1

<sup>a</sup> A to F GTO basis sets; 8, 6, 3, 1 means 8s, 6p, 3d, 1f. STO basis G: 12s, 11p, 11d, 11f, 8g, H: 15s, 13p, 12d, 11f, 10g, 5h.

CuH obtained with the same GTO basis. It is surprising how little the pair-correlation energies change between Cu<sup>+</sup> and CuH. Only those pairs which involve 3d AOs are affected to a significant extent. The overall change in the correlation

energy of the Cu<sup>+</sup> core is 19  $mE_h$  on conventional MP2 level and 31  $mE_h$  with MP2-R12.

Most striking is the good agreement between the MP2-R12/A calculations with STO and GTO basis sets, for Cu<sup>+</sup>,

TABLE XI. MP2 pair correlation energies for the ground states of Zn and Zn<sup>2+</sup>, negative in millihartree.

	Zn				Zn <sup>2+</sup>		
	MP2 STO	MP2 Extrap. <sup>a</sup>	MP2-R12/A STO	MP2-R12/A GTO	MP2 STO	MP2 Extrap. <sup>a</sup>	MP2-R12/A STO
1s <sup>2</sup>	32.47	36.54	36.69	36.17	32.29	36.83	36.45
1s2s	6.50	7.23	7.20	6.99	6.44	7.21	7.08
1s3s	0.99	1.10	1.04	1.05	0.98	1.20	1.08
1s4s	0.04	0.04	0.04	0.05	...	...	...
2s <sup>2</sup>	9.75	10.68	10.64	10.62	10.26	10.68	10.69
2s3s	3.39	3.73	3.62	3.54	3.54	4.01	3.66
2s4s	0.17	0.19	0.17	0.16	...	...	...
3s <sup>2</sup>	5.12	6.04	5.97	6.27	5.88	6.22	6.21
3s4s	0.82	0.95	0.83	0.83	...	...	...
4s <sup>2</sup>	24.55	25.53	26.04	26.03	...	...	...
1s2p	36.02	38.16	38.00	39.47	36.72	38.20	38.10
1s3p	4.29	4.56	4.58	4.61	4.37	4.56	4.47
2s2p	59.01	65.76	65.45	65.00	62.75	65.76	65.57
2s3p	12.48	13.56	13.36	12.87	13.16	13.56	13.51
3s2p	14.68	15.72	15.46	13.69	15.10	15.72	15.40
3s3p	34.65	41.67	41.81	42.78	40.39	42.48	42.78
4s2p	0.91	0.95	0.91	0.79	...	...	...
4s3p	6.01	6.51	6.03	5.95	...	...	...
1s3d	0.69	0.64	0.73	0.46	0.58	0.64	0.58
2s3d	17.98	21.00	20.41	22.66	20.07	21.00	20.76
3s3d	66.99	81.90	80.65	89.35	81.37	83.60	85.35
4s3d	55.98	57.00	56.23	54.53	...	...	...
2p <sup>2</sup>	184.32	185.89	191.22	203.56	186.23	185.89	190.44
2p3p	55.88	63.40	57.65	54.09	56.67	65.00	57.64
3p <sup>2</sup>	73.94	78.88	78.68	81.48	75.32	78.98	78.98
2p3d	83.57	86.34	84.06	81.31	85.22	88.35	86.84
3p3d	312.54	327.86	322.84	336.18	313.74	326.37	326.17
3d <sup>2</sup>	503.87	516.76	511.34	532.51	496.40	507.94	506.94
$\Sigma$	1602.5	1698.7	1678.4	1733.0	1547.5	1604.2	1598.4

<sup>a</sup>Ref. 25, 26. Basis STO: minimal 12s, 12p, 12d, 10f, 10g, 8h up to 16s, 16p, 16d, 15f, 12g, 10h; Basis GTO: 20s, 15p, 8d, 2f.

TABLE XII. Partial-wave increments for two  $3d^2$  pairs for Zn, negative in millihartree.

$l, l'$	$^1S$		$^1D$	
	MP2	MP2-R12/A	MP2	MP2-R12/A
0 0	0.94	1005.38	...	...
0 2	...	...	2.75	5048.87
1 1	4.11	-171.62	3.73	-484.54
1 3	...	...	2.72	276.92
2 2	15.63	-788.88	30.84	-4764.27
2 4	...	...	2.17	-0.92
3 3	18.37	+1.74	26.31	2.12
3 5	...	...	2.57	-0.59
4 4	4.08	+0.04	3.72	0.56
5 5	1.41	-0.05	1.00	0.27

$Zn^{2+}$ , and Zn, although the STO basis sets contained up to  $i$  functions ( $l = 6$ ), the GTO basis sets only up to  $f$  functions, i.e., the GTO basis sets didn't satisfy the requirement outlined in Appendix A.

Anyhow this observation is consistent with the partial wave expansion in Table XII. In our GTO calculation the sum of the pair correlation energies of  $3d^2$  pairs in Zn is overestimated by about  $20 mE_h$ , which appears to be mainly due to the truncation at  $f$  AOs. Compared to the magnitude of the total correlation energy this error is rather small and we can conclude that truncation at  $f$  AOs is tolerable even for systems with occupied  $d$  AOs.

Neutral zinc (Table XI) is similar to  $Zn^{2+}$ , even as far as the pairs  $2p^2$  and  $2p3p$  are concerned. The differences

between  $Zn^{2+}$  and Zn resembles somewhat those between isolated  $Cu^+$  and the  $Cu^+$  core in CuH, but they are slightly larger.

Our results for the Kr ground state are found in Table XIV. We have not made extensive basis saturation tests, so the values may be somewhat less reliable than for the other atoms in this study. Reference values from the literature are unknown. It is a different story, of course, that for atoms as heavy as Kr nonrelativistic quantum theory is not the basis of a good description.

## VII. CONCLUSIONS

An important message of the present paper is found in Table XV, where the percentage of the estimated exact MP2 correlation energies  $E^{(2)}$  accounted for in various approximations are collected. One sees that MP2-R12/A(STO) overestimates  $E^{(2)}$  by at most a few tenths of 1%, while MP2-R12/B(STO) is even closer to 100%, but underestimating  $E^{(2)}$ . This can be said for the atoms He to Ca, where sufficiently accurate estimates of the exact  $E^{(2)}$  are available. For the atoms  $Zn^{2+}$ , Zn,  $Cu^+$ , and Kr we have artificially set the MP2-R12/A results to 100%. Conventional STO calculations yield (except for He and Be where they are better) between 95% and 98% of  $E^{(2)}$ . The results for  $Zn^{2+}$ , Zn,  $Cu^+$ , Kr are somewhat better because here  $i$  functions were included. Conventional GTO calculations (again with the exception of He and Be) yield between 73% and 90% of  $E^{(2)}$  and this for basis sets which are close to the

TABLE XIII. MP2 pair energies for the ground state of  $Cu^+$  and the  $Cu^+$  "core" in CuH.

	$Cu^+$				CuH		
	MP2 STO	MP2 Extrap. <sup>a</sup>	MP2-R12/A STO	MP2-R12/A GTO	MP2 GTO	MP2-R12/A GTO	MP2 GTO
$1s^2$	34.10		36.60	36.20	30.40	36.20	30.40
$1s2s$	6.77		7.19	6.91	5.96	6.91	5.95
$1s3s$	1.01		1.08	1.02	0.90	1.04	0.91
$2s^2$	10.45		10.81	10.52	7.52	10.51	7.51
$2s3s$	3.60		3.69	3.51	2.79	3.55	2.80
$3s^2$	6.04	6.34	6.37	6.43	4.39	6.36	4.33
$1s2p$	37.01		38.04	38.77	23.03	38.74	22.99
$1s3p$	4.30		4.40	4.30	2.59	4.31	2.60
$2s2p$	63.72		66.10	66.79	34.57	66.64	34.43
$2s3p$	13.13		13.37	12.88	10.16	12.88	10.16
$3s2p$	15.40		15.70	14.11	11.83	14.19	11.85
$3s3p$	41.92	43.80	44.31	44.32	28.40	44.37	28.09
$1s3d$	0.51		0.51	0.86	0.18	0.84	0.17
$2s3d$	18.15	19.05	18.27	18.44	10.31	18.10	9.74
$3s3d$	81.82	82.25	84.20	90.15	59.58	85.44	55.19
$2p^2$	188.95		192.73	207.04	148.14	207.10	148.17
$2p3p$	57.09		57.92	54.53	46.52	54.75	46.78
$3p^2$	78.07	81.25	81.54	84.12	59.28	84.69	59.68
$2p3d$	77.65	79.15	77.98	72.82	52.08	70.28	49.67
$3p3d$	325.12	335.27	337.87	339.16	235.66	330.55	230.79
$3d^2$	534.52	544.15	538.07	546.25	426.65	529.85	420.03
$\Sigma$	1599.0		1636.8	1658.6	1201.6	1627.3	1182.6

<sup>a</sup> Reference 26. STO basis:  $12s, 12p, 12d, 11f, 9g, 9h, 6i$ ; GTO basis:  $14s, 9p, 5d, 2f$  for Cu,  $10s, 3p, 1d$  for H.

TABLE XIV. MP2 pair energies for the Kr ground state, negative in millihartree.

Pair	MP2 STO	MP2-R12/A STO	Pair	MP2 STO	MP2-R12/A STO
1s <sup>2</sup>	31.98	36.15	3s4p	20.52	20.85
1s2s	6.22	7.10	4s2p	1.96	2.06
1s3s	1.06	1.06	4s3p	9.28	9.57
1s4s	0.11	0.11	4s4p	52.17	56.88
2s <sup>2</sup>	9.53	10.05	1s3d	0.95	0.95
2s3s	3.51	3.65	2s3d	27.18	28.37
2s4s	0.41	0.43	3s3d	68.54	69.12
3s <sup>2</sup>	5.09	5.37	4s3d	35.22	35.95
3s4s	1.67	1.73	2p <sup>2</sup>	173.19	178.51
4s <sup>2</sup>	8.93	9.30	2p3p	57.85	59.22
1s2p	36.50	38.20	2p4p	5.05	5.05
1s3p	5.12	5.34	3p <sup>2</sup>	64.64	68.59
1s4p	0.37	0.37	3p4p	18.51	18.72
2s2p	59.01	62.64	4p <sup>2</sup>	137.85	147.68
2s3p	13.67	14.14	2p3d	111.73	114.69
2s4p	1.15	1.15	3p3d	262.24	276.71
3s3p	14.07	14.58	4p3d	97.08	97.38
3s3p	32.89	35.60	3d <sup>2</sup>	447.13	459.27
			Σ	1822.4	1896.5

STO basis: 12s, 12p, 12d, 11f, 9g, 9h, 6i.

maximum of what one can afford. With the same GTO bases the MP2-R12 results are off the exact  $E^{(2)}$  by less than 1% up to Ca.

One may wonder whether the present approach means a real progress in atomic theory. In fact neither our pair energies nor our total MP2 energies are very much superior to extrapolated values from conventional partial wave expansions. This is certainly not a definite statement. The overall accuracy (errors at present of a few tenths of a percent of the correlation energy) can certainly be pushed further by two orders of magnitude if one abandons the expansions in STOs, with which one reaches too fast near-linear dependencies. Even in the present implementation our method is superior to traditional partial-wave expansions if one wants to go beyond MP2, where one can no longer use different basis sets for different pairs and where the fact that we don't need very large basis sets is a real advantage. Work on these lines is in progress.

Nevertheless the main reason for applying our method to high-performance atomic calculations has been to have

these calculations as benchmarks for our molecular program for which basis saturation tests would have been much harder. With the atomic program we were able to show how the MP2-R12 results converge to the exact (basis set limit) MP2 energies. We were able to demonstrate clearly that the good results on MP2-R12 level with standard Gaussian basis sets were not just a matter of good luck, but that with basis sets which are good for 70% to 90% of the MP2 correlation energy, the MP2-R12 results are off the basis set limits by only a few percent.

One should not deny that especially MP2-R12/A does not furnish an upper bound to the exact second-order energy and that one may overshoot the MP2 energy, and that in some cases there may be a fortunate cancellation of errors. It appears, however, that MP2-R12/B, for which the partial-wave truncation error goes strictly as  $(l + 1)^{-7}$ , behaves in practice as if it were satisfying an upper-bound property.

The MP2-R12 approach is certainly very powerful, but it is not foolproof. For too small or inappropriately chosen basis sets one may get meaningless results.

TABLE XV. Percentage of the estimated exact MP2 energy accounted for.

	$E^{(2)}$	MP2 GTO	MP2 STO	MP2-R12/A STO	MP2-R12/B STO	MP2-R12/A GTO	MP2-R12/B GTO
He	37.364	97.6	98.9	100.03	99.99	100.10	99.98
Be	76.316	95.6	98.5	100.07	99.99	100.32	99.63
Ne	387.8	90.2	97.8	100.03	99.95	100.18	99.05
Mg	426.7	90.6	97.0	100.07	99.93	100.38	99.51
Ar	706.0	85.7	97.1	100.34	99.88	99.84	97.56
Ca	798.3	84.6	96.1	100.06	99.90	100.80	99.09
Cu <sup>+</sup>	1636.75	73.4	97.7	(100.0)		101.33	
Zn <sup>2+</sup>	1598.36		96.8	(100.0)			
Zn	1678.38	74.8	95.5	(100.0)		103.25	
Kr	1896.54		96.1	(100.0)			



## ACKNOWLEDGMENTS

The computations reported here were done on the CYBER 205 of the computer center of the Ruhr-Universität Bochum. We thank the staff of this center for its assistance. Financial support by Deutsche Forschungsgemeinschaft and by Fonds der Chemie is gratefully acknowledged.

## APPENDIX A

## Requirements on the basis to fulfill the completeness relations

Some three-electron integrals that arise in the exact formulation of the theory (see paper I, Sec. IV), have a finite partial-wave expansion. One example is (see I.4.5,6)

$$\begin{aligned} A_{kl}^{km} B_{km}^j &= \langle k(1)l(2) | A(1,2) | \kappa(1)m(2) \rangle \\ &\quad \times \langle \kappa(3)m(4) | B(3,4) | i(3)j(4) \rangle \\ &= \langle k(1)l(2)m(3) | A(1,2)B(1,3) | i(1)m(2)j(3) \rangle \end{aligned} \quad (\text{A1})$$

with  $A$  and  $B$  spherically symmetric operators (e.g.,  $A = r_{12}$ ,  $B = g_{12} = r_{12}^{-1}$ ), and where  $\kappa$  is a member of a complete set of one-electron functions, over which is summed.  $k, l$  and  $m$  refer to occupied AOs. Let the angular momentum quantum numbers of  $i, j, k, l, m$  and  $\kappa$  be  $l_i, l_j, l_k, l_l, l_m$  and  $l_\kappa$ , respectively. Then the triangular inequality requires that there exists some  $L$  with

$$\begin{aligned} |l_k - l_l| &\leq L \leq l_k + l_l, \\ |l_\kappa - l_m| &\leq L \leq l_\kappa + l_m, \\ |l_i - l_j| &\leq L \leq l_i + l_j. \end{aligned} \quad (\text{A2})$$

Combining these inequalities we get

$$\begin{aligned} l_\kappa &\leq l_k + l_l + l_m, \\ l_\kappa &\leq l_i + l_j + l_m. \end{aligned} \quad (\text{A3})$$

We see that if only  $s$  AOs are occupied (i.e., for He, Be) only  $l_\kappa = 0$  contributes to Eq. (A1), i.e., to satisfy the completeness relation it is sufficient to have a basis with a saturated  $s$  part. If the maximum  $l$  value of occupied AOs is  $l = 1$  (i.e., for Ne, Mg, Ar, Ca) the maximum required  $l_\kappa$  is  $l = 3$ , i.e., the basis must include  $f$  functions (this only for the correlation of  $p^2$  pairs, for  $sp$  pairs  $l = 2$  is sufficient). If  $d$  AOs are occupied (in  $\text{Zn}^{2+}$ , Zn, Kr) we must go up to  $l = 6$ .

We have also to consider four-electron integrals, like (I.4.9d,e) (I.4.11b). It is sufficient to consider only one of these examples, since the argument is completely analogous for the others. Take

$$\begin{aligned} A_{mn}^{\kappa\lambda} B_{\alpha\lambda}^j C_{kp}^{\kappa\lambda} &= \langle mn | A_{12} | \kappa\lambda \rangle \langle \alpha\lambda | B_{34} | ij \rangle \langle kp | C_{56} | kl \rangle \\ &= \langle mnop | A_{12} B_{32} C_{14} | kji l \rangle. \end{aligned} \quad (\text{A4})$$

We conclude from the triangular inequality in the second and third factor that

$$l_\lambda \leq l_i + l_j + l_o, \quad (\text{A5})$$

$$l_\kappa \leq l_k + l_l + l_p.$$

The same condition on the one-electron basis, which justifies the completeness insertion in (A1) hence justifies the analogous insertion in Eq. (A4).

## APPENDIX B

## Choice of the parameters of the STO basis

We start from a basis optimized for SCF calculations and we augment this by other basis functions that should well account for correlation effects and that should satisfy the required completeness insertions. The following formal considerations are useful in order to find the right orbital parameters.

Let us first consider a model problem. Consider the overlap integral between two STOs for  $l_1 = l_2$ .

$$S = \frac{(n_1 + n_2)!}{[(2n_1)!(2n_2)!]^{1/2}} \frac{(2\alpha_1)^{n_1 + 1/2} (2\alpha_2)^{n_2 + 1/2}}{(\alpha_1 + \alpha_2)^{n_1 + n_2 + 1}}. \quad (\text{B1})$$

The maximum  $S = 1$  is, of course, reached for  $n_1 = n_2$  and  $\alpha_1 = \alpha_2$ . Let us now fix  $n_1, n_2$  and  $\alpha_1$  and determine  $\alpha_2$  such that  $S(\alpha_2)$  reaches its maximum. This is realized for

$$\alpha_2 = \alpha_1 \frac{2n_2 + 1}{2n_1 + 1}. \quad (\text{B2})$$

Insertion of Eq. (B2) into (B1) and use of the Stirling formula

$$x^x \approx x! e^x (2\pi x)^{-1/2} \quad (\text{B3})$$

which is accurate within a few percent even for small  $x$ , leads to

$$S_{\max} \approx [(2n_1 + 1)(2n_2 + 1)]^{1/4} (n_1 + n_2 + 1)^{-1/2}. \quad (\text{B4})$$

For  $n_1 = n_2$  this is equal to 1, while for  $n_2 \gg n_1$  we get

$$S_{\max} \approx [2(2n_1 + 1)/(n_2 + 1)]^{1/4} + O(n_2^{-2}). \quad (\text{B5})$$

This integral depends weakly on  $n_2$ , it vanishes as  $n_2^{-1/4}$ .

We don't want to maximize overlap integrals but rather electron interaction integrals or products of such integrals. The conventional second-order energy of the  $a(1)a(2)$  pair is determined by the expression

$$\sum_b \left| \langle a(1)a(2) | \frac{1}{r_{12}} | b(1)b(2) \rangle \right|^2 / (2\epsilon_a - 2\epsilon_b). \quad (\text{B6})$$

We choose the basis  $\{b\}$  so that a single term with a given basis function gets its maximum value. The matrix elements in Eq. (B6) are sums of products of radial integrals of the form

$$g_k = \langle a(1)a(2) | \frac{r_{12}^k}{r_{12}^{k+1}} | b(1)b(2) \rangle \quad (\text{B7})$$

with angular factors. Only the radial factors depend on  $\alpha_b$ . The asymptotic expansion of the integral (B7) in powers of  $k^{-1}$  has the leading term

$$\begin{aligned} &\frac{1}{k} \int r^{2(n_a + n_b)} e^{-2(\alpha_a + \alpha_b)r} dr N_a^2 N_b^2 \\ &= \frac{1}{k} \frac{(2n_a + 2n_b)!}{(2\alpha_a + 2\alpha_b)^{2n_a + 2n_b + 1}} \frac{(2\alpha_a)^{2n_a + 1} (2\alpha_b)^{2n_b + 1}}{(2n_a)!(2n_b)!}. \end{aligned} \quad (\text{B8})$$

Maximization with respect to  $\alpha_2$  leads (independently of  $k$ ) to

$$\alpha_b = \alpha_a \frac{n_b + 1/2}{n_a}. \quad (\text{B9})$$

If we want to maximize (in absolute value) a term in the expression with respect to  $\alpha_2$  for  $n_b \gg n_a$  we get

$$\alpha_b = \alpha_a \frac{n_b}{n_a + 1/2}. \quad (\text{B10})$$

A result symmetric in  $a$  and  $b$  is obtained if we require that the product

$$\langle a(1)a(2) | \left( \frac{1}{r_{12}} \right)_k | b(1)b(2) \rangle \times \langle b(1)b(2) | (r_{12})_k | a(1)a(2) \rangle \quad (\text{B11})$$

is maximized, namely

$$\alpha_b = \alpha_a \frac{n_b + 1/2}{n_a + 1/2}. \quad (\text{B12})$$

We are also interested in a generalization of Eq. (B11)

$$\langle a(1)b(2) | \left( \frac{1}{r_{12}} \right)_k | c(1)d(2) \rangle \times \langle c(1)d(2) | (r_{12})_k | a(1)b(2) \rangle. \quad (\text{B13})$$

Let  $n_a, n_b, n_c, n_d$  as well as  $\alpha_a, \alpha_b, \alpha_c$  be given. The optimum  $\alpha_d$  is then

$$\alpha_d = (\alpha_a + \alpha_b + \alpha_c) \frac{2n_d + 1}{2n_a + 2n_b + 2n_c + 3}. \quad (\text{B14})$$

The leading terms of the  $(1/k)$  expansion of all these expressions are essentially weighted overlap integrals between electron densities, the densities  $|a(1)|^2$  and  $|b(1)|^2$  should, e.g., have maximum overlap. From the overlap between orbitals we know that the maximum overlap is achieved if the principal quantum numbers  $n_1$  and  $n_2$  agree. Now it is usually not possible to choose, e.g.,  $n_a = n_b$ , since the orbitals differ in the angular quantum number. For a given  $1s$  AO one cannot choose the corresponding  $1p$  or  $1d$  AO, but one has to take  $2p$  and  $3d$ . This is less fortunate for the overlap, but can in part be compensated by choosing the appropriate  $\alpha_b$ .

It is somewhat surprising (see Appendix B of part III), that the same relations between the optimized exponents (B11) and (B12) also hold for GTOs.

Our basis sets were built upon SCF sets from the literature, usually from Clementi and Roetti,<sup>27</sup> for Ar and Ca from Sekiya and Tatewaki.<sup>28</sup>

## APPENDIX C

### Matrix elements of the $U$ operator

The operator  $U_{12}$  given by Eq. (2.16) is neither hermitian nor antihermitean. It is recommended to evaluate the matrix elements of its hermitean and antihermitean parts separately. Going back to the original definition of  $U_{12}$ :

$$U_{12} = r_{12}^{-1} - \frac{1}{4} [\nabla_1^2 + \nabla_2^2, r_{12}] \quad (\text{C1})$$

we see that

$$\begin{aligned} U_{12} &= U_{12}^+ + U_{12}^-; \\ U_{12}^+ &= r_{12}^{-1}; \\ U_{12}^- &= -\frac{1}{4} [\nabla_1^2 + \nabla_2^2, r_{12}]. \end{aligned} \quad (\text{C2})$$

The matrix elements of the hermitean part are hence simply

those of  $r_{12}^{-1}$ , which are needed anyway. For the antihermitean part we can take

$$\begin{aligned} \langle \Psi_1 | U_{12}^- | \Psi_2 \rangle &= -\frac{1}{4} \langle (\nabla_1^2 + \nabla_2^2) \Psi_1 | r_{12} | \Psi_2 \rangle \\ &\quad + \frac{1}{4} \langle \Psi_1 | r_{12} | (\nabla_1^2 + \nabla_2^2) \Psi_2 \rangle, \end{aligned} \quad (\text{C3})$$

i.e., we first evaluate  $(\nabla_1^2 + \nabla_2^2) \Psi_k$  and then take matrix elements of  $r_{12}$ .

Some simplification of Eq. (C3) is possible. Let us first decompose  $\nabla^2$  into its angular and radial parts

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{l}^2}{r^2}. \quad (\text{C4})$$

The angular contribution to Eq. (C3) is

$$\begin{aligned} \frac{1}{4} \langle \Psi_1 | \left( \frac{\hat{l}_1^2}{r_1^2} + \frac{\hat{l}_2^2}{r_2^2} \right) | r_{12} | \Psi_2 \rangle \\ - \frac{1}{4} \langle \Psi_1 | r_{12} | \left( \frac{\hat{l}_1^2}{r_1^2} + \frac{\hat{l}_2^2}{r_2^2} \right) | \Psi_2 \rangle. \end{aligned} \quad (\text{C5})$$

This is evaluated easily for STOs since

$$(\hat{l}_1^2 / r_1^2) \chi_{nlm}(r_1) = l(l+1) \chi_{n-2,lm}. \quad (\text{C6})$$

The radial contribution to  $U_{12}^-$

$$U_{12}^- r = -\frac{1}{4} \left[ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2}, r_{12} \right] \quad (\text{C7})$$

is reformulated. We consider only the part involving  $r_1$

$$\begin{aligned} \langle \Psi_1 | \left[ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1}, r_{12} \right] | \Psi_2 \rangle \\ = \langle \Psi_1 | \frac{2}{r_1} \frac{\partial r_{12}}{\partial r_1} + \frac{\partial^2 r_{12}}{\partial r_1^2} + 2 \frac{\partial r_{12}}{\partial r_1} \frac{\partial}{\partial r_1} | \Psi_2 \rangle \\ = \langle \Psi_1 | \frac{\partial}{\partial r_1} \frac{\partial r_{12}}{\partial r_1} + \frac{\partial r_{12}}{\partial r_1} \frac{\partial}{\partial r_1} + \frac{2}{r_1} \frac{\partial r_{12}}{\partial r_1} | \Psi_2 \rangle \\ = \langle \Psi_1 | \left( -\frac{\partial}{\partial r_1} \right)^\dagger \frac{\partial r_{12}}{\partial r_1} + \frac{\partial r_{12}}{\partial r_1} \frac{\partial}{\partial r_1} | \Psi_2 \rangle \\ = -\langle \frac{\partial \Psi_1}{\partial r_1} | \frac{\partial r_{12}}{\partial r_1} | \Psi_1 \rangle + \langle \Psi_1 | \frac{\partial r_{12}}{\partial r_1} | \frac{\partial \Psi_2}{\partial r_1} \rangle. \end{aligned} \quad (\text{C8})$$

We have used that

$$-\left( \frac{\partial}{\partial r_1} \right)^\dagger = \frac{\partial}{\partial r_1} + \frac{2}{r_1}. \quad (\text{C9})$$

We further note that

$$\frac{\partial r_{12}}{\partial r_1} = \frac{r_1 - r_2 \cos \vartheta_{12}}{r_{12}}. \quad (\text{C10})$$

From this one gets the partial-wave expansion of  $U_{12}^- r$

$$\begin{aligned} U_{12}^- r = -\sum_k \left\{ A_k \frac{\partial}{\partial r_>} - \left( \frac{\partial}{\partial r_>} \right)^\dagger A_k + B_k \frac{\partial}{\partial r_<} \right. \\ \left. - \left( \frac{\partial}{\partial r_<} \right)^\dagger B_k \right\} P_k(\cos \vartheta), \end{aligned} \quad (\text{C11})$$

$$A_k = \frac{l-1}{2l-1} \frac{r_<^l}{r_>^l} - \frac{l+1}{2l+3} \frac{r_<^{l+2}}{r_>^{l+2}}, \quad (\text{C12a})$$

$$B_k = \frac{l+2}{2l+3} \frac{r_<^{l+1}}{r_>^{l+1}} - \frac{l}{2l-1} \frac{r_<^{l-1}}{r_>^{l-1}}. \quad (\text{C12b})$$

- <sup>1</sup>T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- <sup>2</sup>R. N. Hill, *J. Chem. Phys.* **83**, 1173 (1985).
- <sup>3</sup>W. Kutzelnigg, *Theoret. Chim. Acta* **68**, 445 (1985).
- <sup>4</sup>W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).
- <sup>5</sup>W. Klopper and W. Kutzelnigg, *J. Chem. Phys.* **94**, 2020 (1991).
- <sup>6</sup>W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).
- <sup>7</sup>W. Klopper and W. Kutzelnigg, in *Quantum Chemistry—Basic Aspects, Actual Trends*, edited by R. Carbo, *Studies in Physical and Theoretical Chemistry* (Elsevier, Amsterdam, 1989), Vol. 62, p. 45.
- <sup>8</sup>W. Klopper and W. Kutzelnigg, *J. Phys. Chem.* **94**, 5625 (1990).
- <sup>9</sup>C. C. J. Roothaan (private communication).
- <sup>10</sup>W. Kutzelnigg and J. D. Morgan (to be published).
- <sup>11</sup>W. Kutzelnigg, M. Schindler, W. Klopper, S. Koch, U. Meier, and H. Wallmeier, in *Super Computer Simulations in Chemistry*, edited by M. Dupuis, *Lecture Notes in Chemistry* (Springer, Berlin, 1986), Vol. 44, p. 55.
- <sup>12</sup>P. Malinowski, M. Polasik, and K. Jankowski, *J. Phys. B* **12**, 2965 (1979).
- <sup>13</sup>B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, *J. Chem. Phys.* **78**, 1420 (1983); **79**, 554 (1983); **81**, 368, 2723 (1984); S. A. Alexander, H. J. Monkhorst, and K. Szalewicz, *ibid.* **85**, 5821 (1986), **87**, 3976 (1987), **89**, 355 (1988).
- <sup>14</sup>K. Jankowski and P. Malinowski, *Phys. Rev. A* **21**, 45 (1980).
- <sup>15</sup>I. Lindgren and S. Salomonsen, *Phys. Scr.* **21**, 335 (1980).
- <sup>16</sup>G. A. Petersson, A. K. Yee, and A. Bennett, *J. Chem. Phys.* **83**, 5105 (1985).
- <sup>17</sup>K. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. J. Monkhorst, *J. Chem. Phys.* **85**, 3964 (1986).
- <sup>18</sup>B. Jeziorski (private communication).
- <sup>19</sup>H. Sekino and Y. Ishikawa, *Int. J. Quant. Chem. Symp.* **23**, 339 (1989).
- <sup>20</sup>S. Salomonson and P. Öster, *Phys. Rev. A* **40**, 5559 (1989).
- <sup>21</sup>K. Jankowski, P. Malinowski, and M. Polasik, *J. Phys. B* **12**, 3157 (1979).
- <sup>22</sup>K. Jankowski, P. Malinowski, and M. Polasik, *Acta Phys. Pol. A* **74**, 207 (1988).
- <sup>23</sup>B. H. Wells and S. Wilson, *J. Phys. B* **19**, 2411 (1986).
- <sup>24</sup>V. Termath, *Diplomarbeit*, Ruhr-Universität Bochum, 1988.
- <sup>25</sup>K. Jankowski, P. Malinowski, and M. Polasik, *J. Chem. Phys.* **76**, 448 (1982).
- <sup>26</sup>K. Jankowski, P. Malinowski, and M. Polasik, *J. Chem. Phys.* **82**, 841 (1985).
- <sup>27</sup>E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974).
- <sup>28</sup>M. Sekiya and H. Tatewaki, *Theoret. Chim. Acta* **71**, 149 (1987).