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# Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. I. General theory

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The matrix elements needed in a CI-SD, CEPA, MP2, or MP3 calculation with linear $r_{12}$-dependent terms for closed-shell states are derived, both exactly and in a consistent approximate way. The standard approximation $B$ guarantees that in the atomic case the error due to truncation of the basis at some angular momentum quantum number $L$ goes as $\sim L^{-7}$, at variance with $L^{-3}$ in conventional calculations (without $r_{12}$ terms). Another standard approximation $A$ has errors $\sim L^{-5}$, but is simpler and—for moderate basis sets—somewhat better balanced. The explicit expressions for Møller–Plesset perturbation theory of second and third order with linear $r_{12}$ terms (MP2-R12 and MP3-R12, respectively) are explicitly given in the two standard approximations.

## I. INTRODUCTION

The slow convergence of the traditional configuration interaction (CI) expansion is due[1-3] to the inability of this expansion to describe the correlation cusp[4]

$$\lim_{r_{12}\to 0}\left(\frac{\partial\Psi}{\partial r_{12}}\right)_{av} = \tfrac{1}{2}\Psi(r_{12}=0), \tag{1.1}$$

which itself is a direct consequence of the singularity of the Coulomb repulsion. It implies that the exact wave function is linear in $r_{12}$ for small $r_{12}$.[5]

For two-electron atoms the CI expansion can be done in two steps. In step 1 one expands the wave function into partial wave contributions, which is particularly simple for an $S$ state

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_l \psi_l(r_1,r_2)P_l(\cos\vartheta_{12}), \tag{1.2}$$

and then one further expands each partial wave amplitude as

$$\psi_l(r_1,r_2) = \sum_{p,q} c^l_{pq}\chi_p(r_1)\chi_q(r_2). \tag{1.3}$$

Both expansions (1.2) and (1.3) are slowly convergent. Schwartz[5] has shown long ago that the second-order contributions (in terms of a $1/Z$ expansion) $E_l^{(2)}$ to the partial wave increments of the energy $E^{(2)}$ of the He ground state go as

$$E_l^{(2)} = -(45/256)(l+\tfrac{1}{2})^{-4} + O\{(l+\tfrac{1}{2})^{-6}\}, \tag{1.4}$$

and Lakin[6] has pointed out that the partial wave increments $E_l$ (nonexpanded in $1/Z$) are $O[(l+\frac{1}{2})^{-4}]$ as well. This means that the error of a CI expansion truncated at some maximum $l$ value $L$ goes as $(L+1)^{-3}$, which is pretty slow.

The convergence of the expansion (1.3) has not yet found a mathematical analysis, but numerical experience clearly indicates[3] that this expansion converges more and more slowly for increasing $l$ due to the increasingly singular nature of the partial wave contribution $r_<^k/r_>^{k+1}$ to $r_{12}^{-1}$. This means that evaluating the $E_l$ numerically with the expansion (1.3) for sufficiently high $l$ in order to be in the asymptotic region for the partial wave expansion is not a safe procedure. In fact fast convergence for a single partial wave is only possible if one expresses $\psi_l$ as a function of $r_>$ and $r_<$.[7,8]

The convergence of the partial wave expansion (1.2) is speeded up considerably if one allows explicitly for terms linear in $r_{12}$, i.e., if one replaces (1.2) by[3]

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \tfrac{1}{2}r_{12}\phi(\mathbf{r}_1,\mathbf{r}_2) + \chi, \tag{1.5}$$

$$\chi = \sum_l \chi_l(r_1,r_2)P_l(\cos\vartheta_{12}), \tag{1.6}$$

where $\phi$ is some single-particle model reference function, e.g., the eigenfunction of the bare nuclear Hamiltonian (without electron interaction) or a Hartree–Fock-type wave function. The second-order perturbation energy $E^{(2)}$ now consists of a term $A^{(2)}$ that can be evaluated in closed form, and partial wave increments $\tilde{E}_l^{(2)}$ that go as $(l+\frac{1}{2})^{-8}$ rather than $(l+\frac{1}{2})^{-4}$.[3] This can be understood in the following way. Insert the ansatz (1.5) into the inhomogeneous differential equation which determines the first-order wave function $\psi^{(1)}$ (with the bare nuclear Hamiltonian as $H_0$).

One gets

$$(H_0 - E_0)\chi^{(1)} = -(U_{12} - E_1)\phi, \tag{1.7}$$

i.e., $\chi^{(1)}$ satisfies the same equation as $\psi^{(1)}$, just with the interaction potential $g_{12} = r_{12}^{-1}$ replaced by the "residual interaction operator" $U_{12}$:

$$U_{12} = [T_1 + T_2, \tfrac{1}{2}r_{12}] + g_{12} = -\frac{1}{2}\frac{\mathbf{r}_{12}}{r_{12}}\cdot(\nabla_1 - \nabla_2). \tag{1.8}$$

The operator $U_{12}$ is much less singular at $r_{12}=0$ than is $g_{12}$. In the special case of the ground state of He-like ions one finds[3]

$$U_{12}\phi = Z\frac{r_1+r_2}{r_{12}}\sin^2\frac{\vartheta_{12}}{2}\phi, \tag{1.9}$$

which vanishes for $r_{12} \to 0$.

A similar speed-up of the convergence has also been found in CI calculations of two-electron atoms.[3] The next step was a generalization of this method to atoms or molecules with more than two electrons. Some preliminary applications on second-order Møller–Plesset level[9-11] were very encouraging. This is confirmed by the numerical results in the forthcoming papers of this series.[12,13]

In this paper the theoretical background for many-electron closed shell calculations with linear $r_{12}$ terms will be given, i.e., we derive all matrix elements needed in Møller-Plesset theory to second or third order, in configuration interaction with singly and doubly substituted configurations (CI-SD) and the corresponding (size-extensive) coupled-electron pair (CEPA) calculations.

On this level in addition to two-electron integrals (traditional ones and new ones), three-electron integrals like ($g_{12} = r_{12}^{-1}$)

$$\langle \varphi(1,2,3) | r_{12} g_{13} | \varphi(1,2,3) \rangle, \tag{1.10}$$

$$\langle \varphi(1,2,3) | r_{12} g_{13} r_{23} | \varphi(1,2,3) \rangle, \tag{1.11}$$

and four-electron integrals like

$$\langle \varphi(1,2,3,4) | r_{12} g_{23} r_{34} | \varphi(1,2,3,4) \rangle \tag{1.12}$$

arise. Closed formulas for these integrals are available for atomic calculations in terms of Slater-type orbitals (STOs),[14] but these formulas are complicated and their evaluation is time consuming. For molecules in terms of Gaussians, formulas have been derived[15,16] that involve a one-dimensional numerical integration for integrals of type (1.10) and (1.12) and a two-dimensional numerical integration for type (1.11). Again the evaluation is time consuming.

However, even if fast procedures for the evaluation of these integrals were available, one would have to face the problem of the large number of these integrals; while that of two-electron integrals is $\sim N^4$, there are $\sim N^6$ three-electron and $\sim N^8$ four-electron integrals. The storing and manipulating of these integrals could be handled only for extremely small basis sets.

We have therefore decided to avoid three and four electron integrals entirely, and how we did so is a key feature of the present method. We have even managed to avoid two-electron integrals of the type

$$\langle \varphi(1,2) | r_1^{-1} r_{12} | \varphi(1,2) \rangle \tag{1.13}$$

which are time consuming in the molecular case because they require a one-dimensional numerical integration.[15]

In a complete basis it is always possible to express three-electron integrals of the types needed here, in terms of two-electron integrals, e.g.,

$$\begin{aligned}
&\langle \varphi_1(1)\varphi_2(2)\varphi_3(3) | r_{12} g_{13} | \varphi_1(1)\varphi_2(2)\varphi_3(3) \rangle \\
&\quad = \sum_{p,q,r} \langle \varphi_1(1)\varphi_2(2)\varphi_3(3) | r_{12} | \varphi_p(1)\varphi_q(2)\varphi_r(3) \rangle \\
&\qquad \times \langle \varphi_p(1)\varphi_q(2)\varphi_r(3) | g_{13} | \varphi_1(1)\varphi_2(2)\varphi_3(3) \rangle \\
&\quad = \sum_{p,q,r} \langle \varphi_1(1)\varphi_2(2) | r_{12} | \varphi_p(1)\varphi_q(2) \rangle \delta_{r3} \\
&\qquad \times \langle \varphi_p(1)\varphi_r(3) | g_{13} | \varphi_1(1)\varphi_3(3) \rangle \delta_{q2} \\
&\quad = \sum_{p} \langle \varphi_1(1)\varphi_2(2) | r_{12} | \varphi_p(1)\varphi_2(2) \rangle \\
&\qquad \times \langle \varphi_p(1)\varphi_3(2) | g_{12} | \varphi_1(1)\varphi_3(2) \rangle .
\end{aligned} \tag{1.14}$$

If one makes such a "completeness insertion" in terms of a given and hence incomplete basis, one introduces errors. However, the errors are—depending on the type of the integral—of very different magnitude, as can be seen from the study of these integrals in the atomic case in terms of a partial wave expansion. Some integrals have a finite partial wave expansion. Take, e.g., the integral (1.14) and assume that $\varphi_1$, $\varphi_2$, and $\varphi_3$ are all $s$ functions, then only $s$-type $\varphi_p$ functions contribute to the sum on the right-hand side and it is sufficient to have a complete $s$ basis in order to get the exact result. It is relatively realistic to require that a basis is chosen such that its $s$ part is sufficiently close to complete. The four-electron integral (1.12) also has a finite partial wave expansion and is easily evaluated by means of a completeness insertion.

The partial wave expansion of the integral (1.11) does not break off. However, as is shown in the appendix A, its partial wave increments go as $(l+\frac{1}{2})^{-8}$, i.e., the error in truncating the basis at some $L$ goes as $(L+1)^{-7}$. Compared to the truncation error of traditional CI, which is of $O([L+1]^{-3})$, the truncation error introduced by evaluating (1.11) via a completeness insertion is rather small.

This paper is organized as follows. In Sec. II the basic notations are introduced. We use a Fock-space formalism and a tensor notation of matrix elements introduced previously.[17-19] Section III contains the matrix elements needed for a closed-shell CI-SD, CEPA, MP2, or MP3 calculation. However, these expressions contain sums over complete sets that cannot be used directly. In Sec. IV both the exact evaluation of these sums and a hierarchy of approximations are discussed. The so-called "standard approximation" is presented and justified. The matrix elements in the standard approximation are given in Sec. V, where two variants $A$ and $B$ are also presented which differ only for one matrix element. Approximation $B$ is usually superior, but more complicated than approximation $A$. Section VI deals with the elimination of spin while in Secs. VII and VIII the respective expressions for second- and third-order Møller-Plesset theory are given.

## II. NOTATIONS

We choose the following convention for labels of spin-orbitals or the corresponding creation, annihilation, or excitation operators

| | |
|---|---|
| $i,j,k,\ldots$ | occupied in the reference Slater determinant $\phi$ |
| $a,b,c,\ldots$ | unoccupied, but contained in the given basis |
| $p,q,r,\ldots$ | arbitrary, but contained in the given basis |
| $\alpha,\beta,\gamma,\ldots$ | unoccupied, belonging to a complete set |
| $\kappa,\lambda,\mu,\ldots$ | arbitrary, forming a complete basis. |

The basis functions are assumed to be orthonormal, with $(p,q,r,\ldots)$ a subset of $(\kappa,\lambda,\mu,\ldots)$ and $(a,b,c,\ldots)$ a subset of $(\alpha,\beta,\gamma,\ldots)$.

The tensor notation for matrix elements and for excitation operators, introduced previously[17,18] is used

$$X_q^p = \langle q|X|p\rangle, \tag{2.1a}$$

$$Y_{rs}^{pq} = \langle \psi_r(1)\psi_s(2)|Y(1,2)|\psi_p(1)\psi_q(2)\rangle = Y_{sr}^{qp}, \tag{2.1b}$$

$$a_q^p = a^p a_q = a_p^\dagger a_q, \tag{2.2a}$$

$$a_{rs}^{pq} = a^p a^q a_s a_r = a_p^\dagger a_q^\dagger a_s a_r, \tag{2.2b}$$

where $X$ is a one-electron operator, $Y$ a two-electron operator, $a^p = a_p^\dagger$ is a creation and $a_p$ an annihilation operator for the spinorbital $\psi_p$. Antisymmetrized matrix elements are written as

$$\overline{Y}_{rs}^{pq} = Y_{rs}^{pq} - Y_{rs}^{qp}. \tag{2.3}$$

"Excited" configurations—with respect to a closed-shell reference Slater determinant $\phi$—are designated as

$$\phi_i^a = a_i^a\phi; \quad \phi_{ij}^{ab} = a_{ij}^{ab}\phi \tag{2.4}$$

with the adjoints

$$(\phi_i^a)^* = \langle\phi_a^i| = \langle\phi|a_a^i; \quad (\phi_{ij}^{ab})^* = \langle\phi_{ab}^{ij}| = \langle\phi|a_{ab}^{ij}. \tag{2.5}$$

We define (implying the Einstein summation convention over the indices $\alpha,\beta$ independently)

$$\phi_{ij} = \tfrac{1}{2}r_{\alpha\beta}^{ij}a_{ij}^{\alpha\beta}\phi = \tfrac{1}{4}\overline{r}_{\alpha\beta}^{ij}a_{ij}^{\alpha\beta}\phi; \quad \phi^{ij} = (\phi_{ij})^*. \tag{2.6a}$$

The matrix elements of $r_{12}$ are written as

$$r_{\alpha\beta}^{ij} = \langle\psi_\alpha(1)\psi_\beta(2)|r_{12}|\psi_i(1)\psi_j(2)\rangle. \tag{2.6b}$$

The function $\phi_{ij}$ takes care of the necessary term linear in $r_{12}$. We construct a function that is equivalent to $\phi_{ij}$, but orthogonal to all excited configurations expressible in the given basis

$$\tilde{\phi}_{ij} = \tfrac{1}{4}N_{ij}\{\overline{r}_{\alpha\beta}^{ij}a_{ij}^{\alpha\beta} - \overline{r}_{ab}^{ij}a_{ij}^{ab}\}\phi = \tfrac{1}{4}N_{ij}\overline{R}_{\alpha\beta}^{\ ij}a_{ij}^{\alpha\beta}\phi, \tag{2.7}$$

where $N_{ij}$ is a normalization factor, to be determined later, and with

$$R_{\alpha\beta}^{\ ij} = \begin{cases} r_{\alpha\beta}^{ij} & \text{for } \alpha\notin(a,b) \text{ or } \beta\notin(a,b) \\ 0 & \text{for } \alpha\in(a,b) \text{ and } \beta\in(a,b)^i \end{cases} \tag{2.8a}$$

$$\overline{R}_{\alpha\beta}^{\ ij} = R_{\alpha\beta}^{\ ij} - R_{\alpha\beta}^{\ ji}. \tag{2.8b}$$

In a CI-type approach it is recommended to use an orthonormal basis of $n$-electron functions. In Møller–Plesset perturbation theory one prefers an unnormalized counterpart of $\tilde{\phi}_{ij}$, namely

$$\tilde{\tilde{\phi}}_{ij} = \tfrac{1}{4}\overline{R}_{\alpha\beta}^{\ ij}a_{ij}^{\alpha\beta}\phi. \tag{2.9}$$

We shall need operators in normal order in the particle–hole sense and designate them by a tilde like $\tilde{a}_q^p$, $\tilde{a}_{rs}^{pq}$.[18,19] For the operators $a_{ij}^{ab}$, $a_{ab}^{ij}$, $a_{ij}^{\alpha\beta}$, $a_{\alpha\beta}^{ij}$ it makes no difference whether or not one puts the tilde.

The Hamiltonian in the particle–hole picture is (with the Einstein summation convention implied)[18,19]

$$H = E_0 + H^{(1)} + H^{(2)}, \tag{2.10a}$$

$$E_0 = h_i^i + \tfrac{1}{2}(g_{ij}^{ij} - g_{ji}^{ij}); \quad g(1,2) = (r_{12})^{-1}, \tag{2.10b}$$

$$H^{(1)} = f_\lambda^\kappa\tilde{a}_\kappa^\lambda; \quad f_\lambda^\kappa = h_\lambda^\kappa + g_{i\lambda}^{i\kappa} - g_{\lambda i}^{i\kappa}, \tag{2.10c}$$

$$H^{(2)} = \tfrac{1}{2}g_{\mu\nu}^{\kappa\lambda}\tilde{a}_{\kappa\lambda}^{\mu\nu} = \tfrac{1}{4}\overline{g}_{\mu\nu}^{\kappa\lambda}\tilde{a}_{\kappa\lambda}^{\mu\nu}. \tag{2.10d}$$

We assume that the Hartree–Fock energy $E_0$ has been made stationary, which implies the usual Brillouin condition

$$f_a^i = f_i^a = 0. \tag{2.11}$$

We shall also refer to a "generalized Brillouin condition"

$$f_\alpha^i = f_i^\alpha = 0 \tag{2.12a}$$

and an "extended Brillouin condition"

$$f_\beta^\alpha = f_a^\beta = 0. \tag{2.12b}$$

For the justification and the possible use of these conditions see Sec. V.

## III. PRELIMINARY EXPRESSIONS FOR THE MATRIX ELEMENTS

The functions $\phi,\phi_i^a,\phi_{ij}^{ab},\tilde{\phi}_{ij}$ form an orthonormal set provided that

$$\begin{aligned}\langle\tilde{\phi}^{ij}|\tilde{\phi}_{ij}\rangle &= \tfrac{1}{8}N_{ij}^2\overline{R}_{ij}^{\ \alpha\beta}\overline{R}_{\alpha\beta}^{\ ij} \\ &= \tfrac{1}{4}N_{ij}^2\{r_{ij}^{\alpha\beta}r_{\alpha\beta}^{ij} - r_{ij}^{\alpha\beta}r_{\alpha\beta}^{ji} - r_{ij}^{ab}r_{ab}^{ij} + r_{ij}^{ab}r_{ab}^{ji}\} \\ &= 1,\end{aligned} \tag{3.1}$$

which determines $N_{ij}$. As it stands, Eq. (3.1) cannot be used since it involves a formal summation over the complete set $\{\alpha\}$ of virtual orbitals. We shall show in Sec. IV how to evaluate expressions of this type either exactly or in a consistent approximate way.

The matrix elements of the one-particle part $H^{(1)}$ of the Hamiltonian (2.10) in particle–hole formalism are

$$\langle\phi|H^{(1)}|\phi_i^a\rangle = f_i^a = 0, \tag{3.2a}$$

$$\langle\phi|H^{(1)}|\phi_{ij}^{ab}\rangle = 0, \tag{3.2b}$$

$$\langle\phi|H^{(1)}|\tilde{\phi}_{ij}\rangle = 0, \tag{3.2c}$$

$$\langle\phi_c^k|H^{(1)}|\phi_i^a\rangle = \delta_i^k f_a^c - \delta_a^c f_i^k, \tag{3.2d}$$

$$\langle\phi_c^k|H^{(1)}|\phi_{ij}^{ab}\rangle = 0, \tag{3.2e}$$

$$\langle\phi_c^k|H^{(1)}|\tilde{\phi}_{ij}\rangle = 0, \tag{3.2f}$$

$$\begin{aligned}\langle\phi_{cd}^{kl}|H^{(1)}|\phi_{ij}^{ab}\rangle = (\delta_i^k\delta_j^l - \delta_j^k\delta_i^l)(\delta_c^a f_d^b + \delta_d^b f_c^a - \delta_d^a f_c^b \\ - \delta_c^b f_d^a) - (\delta_i^k f_j^l + \delta_j^l f_i^k - \delta_j^k f_i^l \\ - \delta_i^l f_j^k)(\delta_c^a\delta_d^b - \delta_d^a\delta_c^b),\end{aligned} \tag{3.2g}$$

$$\langle\phi_{cd}^{kl}|H^{(1)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{2}(\delta_i^k\delta_j^l - \delta_j^k\delta_i^l)(\overline{R}_{c\beta}^{\ ij}f_d^\beta + \overline{R}_{\alpha d}^{\ ij}f_c^\alpha), \tag{3.2h}$$

$$\begin{aligned}\langle\tilde{\phi}^{kl}|H^{(1)}|\tilde{\phi}_{ij}\rangle = \frac{N_{kl}N_{ij}}{8}\{2(\delta_i^k\delta_j^l - \delta_j^k\delta_i^l)\overline{R}_{kl}^{\ \alpha\delta}f_\delta^\beta\overline{R}_{\alpha\beta}^{\ ij} \\ - (\delta_i^k f_j^l + \delta_j^l f_i^k - \delta_j^k f_i^l - \delta_i^l f_j^k) \\ \times\overline{R}_{kl}^{\ \alpha\beta}\overline{R}_{\alpha\beta}^{\ ij}\}.\end{aligned} \tag{3.2i}$$

Use has been made in (3.2a) and (3.2e) of the Brillouin theorem (2.11). The corresponding expressions for the matrix elements of the two-electron part $H^{(2)}$ are

$$\langle\phi|H^{(2)}|\phi_i^a\rangle = 0, \tag{3.3a}$$

$$\langle\phi|H^{(2)}|\phi_{ij}^{ab}\rangle = \overline{g}_{ij}^{ab}, \tag{3.3b}$$

$$\langle\phi|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{4}\bar{g}_{ij}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij}, \tag{3.3c}$$

$$\langle\phi_c^k|H^{(2)}|\phi_i^a\rangle = \bar{g}_{ci}^{ka}, \tag{3.3d}$$

$$\langle\phi_c^k|H^{(2)}|\phi_{ij}^{ab}\rangle = \delta_i^k\bar{g}_{cj}^{ab} + \delta_j^k\bar{g}_{ic}^{ab} - \delta_c^a\bar{g}_{ij}^{kb} - \delta_c^b\bar{g}_{ij}^{ak}, \tag{3.3e}$$

$$\langle\phi_c^k|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{4}\{\delta_i^k\bar{g}_{cj}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij} + \delta_j^k\bar{g}_{ic}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij} - 2\bar{g}_{ij}^{k\beta}\overline{R}_{c\beta}^{ij}\}, \tag{3.3f}$$

$$\langle\phi_{cd}^{kl}|H^{(2)}|\phi_{ij}^{ab}\rangle = (\delta_c^a\delta_d^b - \delta_d^a\delta_c^b)\bar{g}_{ij}^{kl};\ \text{for } i,j\neq k,l, \tag{3.3g}$$

$$\langle\phi_{cd}^{kl}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{2}\bar{g}_{ij}^{kl}\overline{R}_{cd}^{ij} = 0;\ \text{for } i,j\neq k,l, \tag{3.3h}$$

$$\langle\tilde{\phi}^{kl}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{kl}N_{ij}}{8}\bar{g}_{ij}^{kl}\overline{R}_{kl}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij};\ \text{for } i,j\neq k,l, \tag{3.3i}$$

$$\langle\phi_{cd}^{il}|H^{(2)}|\phi_{ij}^{ab}\rangle = (\delta_c^a\delta_d^b - \delta_d^a\delta_c^b)\bar{g}_{ij}^{il} - \delta_d^b\bar{g}_{cj}^{al} - \delta_c^a\bar{g}_{jd}^{lb} - \delta_d^a\bar{g}_{cj}^{lb} - \delta_c^b\bar{g}_{jd}^{al};\ \text{for } l\neq j, \tag{3.3j}$$

$$\langle\phi_{cd}^{il}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{2}\{-\bar{g}_{cj}^{\alpha l}\overline{R}_{\alpha d}^{ij} - \bar{g}_{jd}^{l\beta}\overline{R}_{c\beta}^{ij}\};\ \text{for } l\neq j, \tag{3.3k}$$

$$\langle\tilde{\phi}^{il}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{il}N_{ij}}{8}\{\overline{R}_{il}^{\gamma\delta}\bar{g}_{ij}^{il}\overline{R}_{\gamma\delta}^{ij} - 2\overline{R}_{il}^{\gamma\delta}\bar{g}_{\gamma j}^{\alpha l}\overline{R}_{\alpha\delta}^{ij}\};\ \text{for } l\neq j, \tag{3.3l}$$

$$\langle\phi_{cd}^{ij}|H^{(2)}|\phi_{ij}^{ab}\rangle = (\delta_c^a\delta_d^b - \delta_d^a\delta_c^b)\bar{g}_{ij}^{ij} + \bar{g}_{cd}^{ab} - \delta_d^b(\bar{g}_{cj}^{aj} + \bar{g}_{ci}^{al}) - \delta_c^a(\bar{g}_{jd}^{jb} + \bar{g}_{id}^{jb}) - \delta_d^a(\bar{g}_{cj}^{jb} + \bar{g}_{ci}^{jb}) - \delta_c^b(\bar{g}_{jd}^{aj} + \bar{g}_{id}^{ai}), \tag{3.3m}$$

$$\langle\phi_{cd}^{ij}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}}{4}\{\bar{g}_{cd}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij} - 2(\bar{g}_{cj}^{\alpha j} + \bar{g}_{ci}^{\alpha i})\overline{R}_{\alpha d}^{ij} - 2(\bar{g}_{jd}^{j\beta} + \bar{g}_{id}^{i\beta})\overline{R}_{c\beta}^{ij}\}, \tag{3.3n}$$

$$\langle\tilde{\phi}^{ij}|H^{(2)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}^2}{8}\{\bar{g}_{ij}^{ij}\overline{R}_{ij}^{\alpha\beta}\overline{R}_{\alpha\beta}^{ij} - 2\overline{R}_{ij}^{\gamma\delta}(\bar{g}_{\gamma j}^{\alpha j} + \bar{g}_{\gamma l}^{\alpha i}) \times\overline{R}_{\alpha\delta}^{ij} + \tfrac{1}{2}\overline{R}_{ij}^{\alpha\beta}\bar{g}_{\alpha\beta}^{\gamma\delta}\overline{R}_{\gamma\delta}^{ij}\}. \tag{3.3o}$$

## IV. EXACT EVALUATION OF THE MATRIX ELEMENTS AND A HIERARCHY OF APPROXIMATIONS

The matrix elements derived in Sec. III contain expressions like [e.g., in Eqs. (3.1), (3.2i), and (3.3c)]

$$A_{ij}^{\alpha\beta}B_{\alpha\beta}^{ij} - A_{ij}^{ab}B_{ab}^{ij}, \tag{4.1}$$

where $(\alpha,\beta,\ldots)$ is a complete set of virtual spinorbitals, $(a,b,\ldots)$ the corresponding set in the given basis. One can either try to evaluate these expressions exactly or to approximate them. The approximations discussed here consist in introducing completeness insertions, e.g., in replacing a sum over a complete basis by a sum over the given basis, e.g., in assuming

$$C_i^\kappa D_\kappa^i \approx C_i^p D_p^i \tag{4.2}$$

($\kappa$ is an arbitrary element of a complete basis, $p$ of the given basis). This type of approximation has at least one merit, namely that it becomes exact in the limit of a complete basis. The crucial point, on which the justification of completeness insertions rests, is how fast the introduced error goes to zero when one extends the basis.

A brute force approach, which may be called the zeroth approximation, consists in inserting completeness relations in terms of the given basis in all matrix elements of Sec. III. This would imply that expressions like Eq. (4.1) are set equal to zero. In this approximation $\phi_{ij}$ as defined by Eq. (2.6) is a linear combination of the $\phi_{ij}^{ab}$, and $\tilde{\phi}_{ij}$ given by Eq. (2.7) vanishes. All the matrix elements involving $\tilde{\phi}_{ij}$ vanish as well and the normalization integral $N_{ij}$ becomes undefined. This "zeroth approximation" is hence nothing but traditional CI without any terms linear in $r_{12}$.

Before we study better approximations let us consider the exact evaluation of Eq. (4.1). We note that (see Fig. 1)

$$A_{kl}^{\alpha\beta}B_{\alpha\beta}^{ij} = A_{kl}^{\kappa\lambda}B_{\kappa\lambda}^{ij} - A_{kl}^{\kappa m}B_{\kappa m}^{ij} - A_{kl}^{n\lambda}B_{n\lambda}^{ij} + B_{kl}^{nm}A_{nm}^{ij}, \tag{4.3a}$$

$$A_{kl}^{ab}B_{ab}^{ij} = A_{kl}^{pq}B_{pq}^{ij} - A_{kl}^{pm}B_{pm}^{ij} - A_{kl}^{nq}B_{nq}^{ij} + B_{kl}^{nm}A_{nm}^{ij}, \tag{4.3b}$$

$$A_{kl}^{\alpha\beta}B_{\alpha\beta}^{ij} - A_{kl}^{ab}B_{ab}^{ij} = A_{kl}^{\kappa\lambda}B_{\kappa\lambda}^{ij} - A_{kl}^{pq}B_{pq}^{ij} - A_{kl}^{\kappa m}B_{\kappa m}^{ij} + A_{kl}^{pm}B_{pm}^{ij} - A_{kl}^{n\lambda}B_{n\lambda}^{ij} + A_{kl}^{nq}B_{nq}^{ij}. \tag{4.3c}$$

The first term on the right-hand side of Eq. (4.3c) is easily evaluated (since $\kappa$ and $\lambda$ refer to a complete basis)

$$A_{kl}^{\kappa\lambda}B_{\kappa\lambda}^{ij} = (AB)_{kl}^{ij} = \langle k(1)l(2)|A(1,2)B(1,2)|i(1)j(2)\rangle. \tag{4.4}$$

The second, fourth, and sixth terms on the right-hand side of Eq. (4.3c) are trivial, since they only involve functions of the "given" basis. In the third and fifth terms on the right-hand side of Eq. (4.3c) sums over the complete basis sets $\{\kappa\}$ or $\{\lambda\}$ and the finite set $\{k\}$ or $\{l\}$ as well are implied. To get closed expressions we write

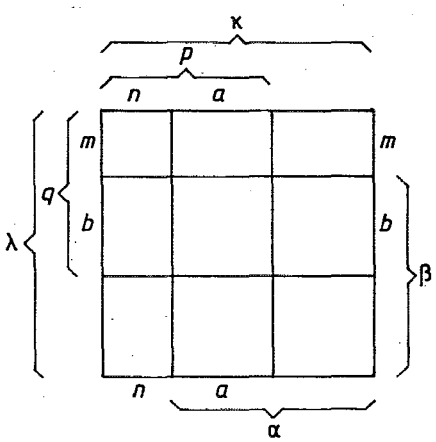


FIG. 1. Illustration of the spaces spanned by basis functions with different labels: $\kappa,\lambda$: arbitrary elements of a complete basis, $p,q$: arbitrary elements of the given basis, $n,m$: functions occupied in the reference Slater determinant $\phi$, $a,b$: elements of the given basis orthogonal to $(m,n)$, $\alpha,\beta$: elements of the complete basis orthogonal to $(m,n)$.

$$A^{\kappa m}_{kl}B^{ij}_{\kappa m} = \langle k(1)l(2)|A(1,2)|\kappa(1)m(2)\rangle \times \langle \kappa(3)m(4)|B(3,4)|i(3)j(4)\rangle \quad (4.5)$$

and take Eq. (4.5) as a sum (over $\kappa$ and $m$) of (factorizing) four-electron integrals. Noting the completeness relation

$$\psi_\kappa(1)\psi^*_\kappa(3) = \delta(\mathbf{r}_1 - \mathbf{r}_3) \quad (4.6)$$

we can rewrite Eq. (4.5) as a three-electron integral. (After replacing $\mathbf{r}_3$ by $\mathbf{r}_1$ we rename $\mathbf{r}_4$ as $\mathbf{r}_3$.)

$$A^{\kappa m}_{kl}B^{ij}_{\kappa m} = \langle k(1)l(2)m(3)|A(1,2)B(1,3)|i(1)m(2)j(3)\rangle. \quad (4.7)$$

(One must still sum over $m$, i.e., over all occupied spinorbitals.)

We proceed similarly with sums over products of three two-electron matrix elements. The first of these [arising, e.g., in Eq. (3.3o)] is that in which a fourfold sum over complete sets is implied:

$$\begin{aligned} A^{\alpha\beta}_{kl}B^{\gamma\delta}_{\alpha\beta}C^{ij}_{\gamma\delta} = {} & A^{\kappa\lambda}_{kl}B^{\mu\nu}_{\kappa\lambda}C^{ij}_{\mu\nu} - A^{m\lambda}_{kl}B^{\mu\nu}_{m\lambda}C^{ij}_{\mu\nu} - A^{\kappa n}_{kl}B^{\mu\nu}_{\kappa n}C^{ij}_{\mu\nu} - A^{\kappa\lambda}_{kl}B^{m\nu}_{\kappa\lambda}C^{ij}_{m\nu} - A^{\kappa\lambda}_{kl}B^{\mu n}_{\kappa\lambda}C^{ij}_{\mu n} + A^{mn}_{kl}B^{\mu\nu}_{mn}C^{ij}_{\mu\nu} + A^{\kappa\lambda}_{kl}B^{mn}_{\kappa\lambda}C^{ij}_{mn} \\ & + A^{m\lambda}_{kl}B^{n\nu}_{m\lambda}C^{ij}_{n\nu} + A^{m\lambda}_{kl}B^{\mu n}_{m\lambda}C^{ij}_{\mu n} + A^{\kappa n}_{kl}B^{m\nu}_{\kappa n}C^{ij}_{m\nu} + A^{\kappa n}_{kl}B^{\mu m}_{\kappa n}C^{ij}_{\mu m} - A^{mn}_{kl}B^{o\nu}_{mn}C^{ij}_{o\nu} \\ & - A^{mn}_{kl}B^{vo}_{mn}C^{ij}_{vo} - A^{m\nu}_{kl}B^{no}_{m\nu}C^{ij}_{no} - A^{\nu m}_{kl}B^{no}_{\nu m}C^{ij}_{no} + A^{nm}_{kl}B^{op}_{nm}C^{ij}_{op} \end{aligned} \quad (4.8)$$

($p$—following $m,n,o$— designates here an occupied rather than an arbitrary spin orbital).

The first term on the right-hand side of Eq. (4.8) is a two-electron matrix element

$$A^{\kappa\lambda}_{kl}B^{\mu\nu}_{\kappa\lambda}C^{ij}_{\mu\nu} = (ABC)^{ij}_{kl}. \quad (4.9a)$$

The sixth and seventh terms on the right-hand side of Eq. (4.8) are also very simple:

$$A^{mn}_{kl}B^{\mu\nu}_{mn}C^{ij}_{\mu\nu} = A^{mn}_{kl}(BC)^{ij}_{mn}. \quad (4.9b)$$

The twelfth to fifteenth terms reduce to three-electron integrals like Eq. (4.7), the sixteenth term finally is a product of three two-electron integrals. There remain three types of expressions, the second to fifth terms, the eighth and eleventh terms, and finally the ninth term. Take the second term [we simplify the notation of Eq. (4.5)]

$$A^{m\lambda}_{kl}B^{\mu\nu}_{m\lambda}C^{ij}_{\mu\nu} = \langle kl|A_{12}|m\lambda\rangle\langle m\lambda|B_{34}|\mu\nu\rangle\langle\mu\nu|C_{56}|ij\rangle = \langle klm|A_{12}B_{32}C_{32}|mji\rangle. \quad (4.9c)$$

It becomes a three-electron integral like Eq. (4.7). For the eighth term we get

$$A^{m\lambda}_{kl}B^{n\nu}_{m\lambda}C^{ij}_{n\nu} = \langle kl|A_{12}|m\lambda\rangle\langle m\lambda|B_{34}|n\nu\rangle\langle n\nu|C_{56}|ij\rangle = \langle klmn|A_{12}B_{32}C_{42}|mjni\rangle, \quad (4.9d)$$

i.e., a four-electron integral.

The ninth term is

$$A^{m\lambda}_{kl}B^{\mu n}_{m\lambda}C^{ij}_{\mu n} = \langle kl|A_{12}|m\lambda\rangle\langle m\lambda|B_{34}|\mu n\rangle\langle\mu n|C_{56}|ij\rangle = \langle klmn|A_{12}B_{32}C_{34}|mnij\rangle, \quad (4.9e)$$

again a four-electron integral, but of a different type.

Two other sums over products of three two-electron matrix elements different from Eq. (4.8) are those with a triple sum over a complete set. The first of these is

$$\begin{aligned} A^{\alpha\beta}_{kl}B^{m\delta}_{m\beta}C^{ij}_{\alpha\delta} = {} & A^{\kappa\lambda}_{kl}B^{m\nu}_{m\lambda}C^{ij}_{\kappa\nu} - A^{\kappa n}_{kl}B^{m\nu}_{mn}C^{ij}_{\kappa\nu} - A^{n\lambda}_{kl}B^{m\nu}_{m\lambda}C^{ij}_{n\nu} \\ & - A^{\kappa\lambda}_{kl}B^{mn}_{m\lambda}C^{ij}_{\kappa n} + A^{no}_{kl}B^{m\nu}_{mo}C^{ij}_{n\nu} + A^{n\lambda}_{kl}B^{mo}_{m\lambda}C^{ij}_{no} \\ & + A^{\kappa n}_{kl}B^{mo}_{mn}C^{ij}_{\kappa o} - A^{np}_{kl}B^{mo}_{mp}C^{ij}_{no} \end{aligned} \quad (4.10a)$$

and the second

$$\begin{aligned} A^{\alpha\beta}_{kl}B^{m\delta}_{\beta m}C^{ij}_{\alpha\delta} = {} & A^{\kappa\lambda}_{kl}B^{m\nu}_{\lambda m}C^{ij}_{\kappa\nu} - A^{\kappa n}_{kl}B^{m\nu}_{nm}C^{ij}_{\kappa\nu} - A^{n\lambda}_{kl}B^{m\nu}_{\lambda m}C^{ij}_{n\nu} \\ & - A^{\kappa\lambda}_{kl}B^{mn}_{\lambda m}C^{ij}_{\kappa n} + A^{no}_{kl}B^{m\nu}_{om}C^{ij}_{n\nu} + A^{n\lambda}_{kl}B^{mo}_{\lambda m}C^{ij}_{no} \\ & + A^{\kappa n}_{kl}B^{mo}_{nm}C^{ij}_{\kappa o} - A^{np}_{kl}B^{mo}_{pm}C^{ij}_{no}. \end{aligned} \quad (4.10b)$$

The first expression on the right-hand side in (4.10a) can be rewritten as

$$A^{\kappa\lambda}_{kl}B^{m\nu}_{m\lambda}C^{ij}_{\kappa\nu} = \langle kl|A_{12}|\kappa\lambda\rangle\langle m\lambda|B_{34}|m\nu\rangle\langle\kappa\nu|C_{56}|ij\rangle = \langle klm|A_{12}B_{32}C_{12}|ijm\rangle, \quad (4.11a)$$

i.e., it is essentially of the type (4.9c).

The third term of Eq. (4.10a) is of the type (4.9d). The fifth to seventh terms are of type (4.7), while the second and fourth terms on the right-hand side of Eq. (4.10a) are of the type

$$A^{\kappa\lambda}_{kl}B^{mn}_{m\lambda}C^{ij}_{\kappa n} = \langle kl|A_{12}|\kappa\lambda\rangle\langle m\lambda|B_{34}|mn\rangle\langle\kappa n|C_{56}|ij\rangle = \langle klmn|A_{12}B_{32}C_{14}|inmj\rangle, \quad (4.11b)$$

very much like Eqs. (4.9d) or (4.9e).

For the first expression on the right-hand side of Eq. (4.10b) we get

$$A^{\kappa\lambda}_{kl}B^{m\nu}_{\lambda m}C^{ij}_{\kappa\nu} = \langle kl|A_{12}|\kappa\lambda\rangle\langle\lambda m|B_{34}|m\nu\rangle\langle\kappa\nu|C_{56}|ij\rangle = \langle klm|A_{12}B_{23}C_{13}|imj\rangle. \quad (4.11c)$$

The other terms in Eq. (4.10b) are of types already discussed.

If one wants to evaluate all the matrix elements of Sec. III rigorously, one has to include three- and four-electron integrals, which is rather tedious and time consuming, both as far as the evaluation of each individual integral and their number is concerned. One would be limited to very small atoms or molecules and to very modest basis sizes.

In order to derive approximations that consist of completeness insertions in terms of the given basis, one must carefully analyze the errors that one makes in doing so. A good measure of this error is the convergence of the partial

wave expansion for atoms. The details are given in Appendix A.

We remember that our matrix elements do not consist of single expressions like the left-hand side of Eq. (4.3a) but rather of differences like on the left-hand side of Eq. (4.3c) of expressions involving sums over *complete* basis sets and the same expressions summed over the *given* basis set.

Let the given basis be saturated up to a given $l$ value and let it not contain functions with higher $l$ values. Further, let $A_{12} = r_{12}$; $B_{12} = g_{12} = 1/r_{12}$. Then the truncation error of Eq. (4.1) is $O(l^{-3})$. If we separate this error according to Eq. (4.3c) into two contributions we get

$$r_{ij}^{\kappa\lambda} g_{\kappa\lambda}^{ij} - r_{ij}^{pq} g_{pq}^{ij} = 1 - r_{ij}^{pq} g_{pq}^{ij} = O(l^{-3}), \tag{4.12a}$$

while

$$-r_{ij}^{\kappa m} g_{\kappa m}^{ij} + r_{ij}^{pm} g_{pm}^{ij} - r_{ij}^{n\lambda} g_{n\lambda}^{ij} + r_{ij}^{nq} g_{nq}^{ij} = 0, \tag{4.12b}$$

provided that $l$ is larger than a required minimum value. The reason for this is that the partial wave expansion of Eq. (4.7) breaks off after some finite $l$.

In what we call the standard approximation we shall hence neglect differences like Eq. (4.12b), and rather take care that the largest $l$ of the basis is large enough and that up to this $l$ the basis can be regarded as saturated.

It turns out that the integrals Eqs. (4.7), (4.9d), (4.9e), and (4.11b) have finite $l$ expansions while the $l$ expansions of Eqs. (4.4), (4.9a,b,c), and (4.11a,c) are infinite. The partial wave increments of Eq. (4.4) go as $\sim l^{-4}$ for $A = r_{12}$, $B = g_{12}$, and as $\sim l^{-6}$ for $A = B = r_{12}$ (see Appendix A), but this does not matter since Eq. (4.4) is easily evaluated in closed form. The same holds for the integrals Eqs. (4.9a,b) or even (4.9c), which is also easily evaluated in closed form, e.g.,

$$\begin{aligned}\langle klm|r_{12}g_{32}r_{32}|mji\rangle &= \langle klm|r_{12}|mji\rangle \\ &= \delta_i^m \langle kl|r_{12}|mj\rangle.\end{aligned} \tag{4.13}$$

Equation (4.11a) can be reduced to the case (4.7) that has a finite $l$ expansion. The only integral that has a nonterminating $l$ expansion and is hard to calculate is Eq. (4.11c). Fortunately this integral has, as shown in the Appendix A (for $A = C = r_{12}$, $B = g_{12}$) partial wave increments that go as $l^{-8}$. This is why in the standard approximation these integrals will be evaluated via completeness insertions, which means that one need not evaluate them at all.

It has so turned out that in the standard approximation only two-electron integrals are needed. In this approximation the truncation error which was $\sim(L+1)^{-3}$ in the standard CI is reduced to $\sim(L+1)^{-7}$, at least to second- and third-order of MP-perturbation theory.

It is consistent with the standard approximation to assume that the generalized and the extended Brillouin theorems (2.12) hold, which simplifies the matrix elements of $H^{(1)}$ considerably. Of course Eq. (2.12a) is satisfied if $\phi$ is the exact Hartree–Fock wave function, i.e., that reached in a basis set limit. We must hence require that the basis is close to saturated on Hartree–Fock level. Equation (2.12b) holds for atoms if the basis is saturated up to a given $l$ value and truncated after this $l$. This is more or less what we need in the standard approximation anyway.

A drawback of the standard approximation is, of course, that it is not strictly variational, i.e., it does not furnish rigorous upper bounds. However, since the convergence to the exact energies is much faster than conventionally, one should not overestimate the importance of staying in the frame of the variation principle.

If one cares for a strictly variational approach, it is not only necessary to evaluate all matrix elements exactly, one must also abandon the generalized and the extended Brillouin theorems. This implies that one also needs integrals like $r_{ij}^{\kappa\lambda} V_{\lambda}^{\mu} r_{\kappa\mu}^{ij}$, where $V$ represents the nuclear attraction potential. These integrals (which are avoided in the standard approximation) require a numerical integration.[15]

## V. MATRIX ELEMENTS IN THE STANDARD APPROXIMATION

In the standard approximation the normalization integral (3.1) becomes ($\overset{\text{sa}}{=}$ always means: in the standard approximation)

$$\langle \tilde{\phi}^{ij}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} \tfrac{1}{4} N_{ij}^2 \{(r^2)_{ij}^{ij} - (r^2)_{ji}^{ij} - r_{ij}^{pq} r_{pq}^{ij} + r_{ij}^{pq} r_{pq}^{ji}\}, \tag{5.1}$$

where

$$(r^2)_{ij}^{ij} = \langle i(1)\, j(2)|r_{12}^2|i(1)\, j(2)\rangle. \tag{5.2}$$

By virtue of the extended Brillouin theorem (2.12b), (3.2h) vanishes

$$\langle \phi_{cd}^{kl}|H^{(1)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} 0. \tag{5.3}$$

The integral (3.2i) vanishes unless at least two labels agree, i.e.,

$$\langle \tilde{\phi}^{il}|H^{(1)}|\tilde{\phi}_{ij}\rangle = -\frac{N_{il}N_{ij}}{8}\{\overline{r}_{il}^{\alpha\beta}\overline{r}_{\alpha\beta}^{ij} - \overline{r}_{il}^{ab}\overline{r}_{ab}^{ij}\} f_j^l, \quad \text{for } l \neq j, \tag{5.4a}$$

$$\langle \tilde{\phi}^{ij}|H^{(1)}|\tilde{\phi}_{ij}\rangle = \frac{N_{ij}^2}{4}\overline{R}_{ij}^{\alpha\delta} f_{\delta}^{\beta} \overline{R}_{\alpha\beta}^{ij} - f_i^i - f_j^j \tag{5.4b}$$

$$\langle \tilde{\phi}^{kl}|H^{(1)}|\tilde{\phi}_{ij}\rangle = 0 \text{ for } k \neq i,j; \quad l \neq i,j. \tag{5.4c}$$

The standard approximation of Eq. (5.4a) is obviously

$$\langle \tilde{\phi}^{il}|H^{(1)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} -\frac{N_{il}N_{ij}}{4}\{(r^2)_{il}^{ij} - (r^2)_{li}^{ij} - r_{il}^{pq} r_{pq}^{ij} + r_{il}^{pq} r_{pq}^{ji}\} f_j^l, \tag{5.5}$$

while for Eq. (5.4b) some reformulations are necessary. We first note that

$$\begin{aligned}[f,r]_{\alpha\beta}^{ij} &= \langle \alpha\beta|[f(1)+f(2), r_{12}]|ij\rangle \\ &= f_{\alpha}^{\rho} r_{\rho\beta}^{ij} + f_{\beta}^{\rho} r_{\alpha\rho}^{ij} - r_{\alpha\beta}^{\rho j} f_{\rho}^{i} - r_{\alpha\beta}^{i\rho} f_{\rho}^{j} \\ &= \langle \alpha\beta|[T(1)+T(2), r_{12}]|ij\rangle \\ &\quad - \langle \alpha\beta|[K(1)+K(2), r_{12}]|ij\rangle \\ &= -2g_{\alpha\beta}^{ij} + 2u_{\alpha\beta}^{ij} + r_{\alpha\beta}^{\rho j} g_{\rho m}^{mi} + r_{\alpha\beta}^{i\rho} g_{\rho m}^{mj} \\ &\quad - g_{\beta m}^{m\rho} r_{\alpha\rho}^{ij} - g_{\alpha m}^{m\rho} r_{\rho\beta}^{ij} \\ &= f_{\alpha}^{\gamma} r_{\gamma\beta}^{ij} + f_{\beta}^{\gamma} r_{\alpha\gamma}^{ij} - r_{\alpha\beta}^{mj} f_m^i - r_{\alpha\beta}^{im} f_m^j\end{aligned} \tag{5.6}$$

with

$$u^{ij}_{\alpha\beta} = \langle \alpha\beta \,|\, U_{12} | ij \rangle = -\tfrac{1}{2} \langle \alpha\beta \,|\, \frac{1}{r_{12}} \mathbf{r}_{12} (\nabla_1 - \nabla_2) | ij \rangle. \quad (5.7)$$

In deriving Eq. (5.6) use has been made of Eqs. (1.8) and of (2.11) and (2.12a).

For $[f,r]^{ij}_{ab}$ a relation analogous to (5.6) is derived, just with $\alpha,\beta,\gamma$ replaced by $a,b,c$. We now use Eqs. (2.12b) and (5.6) to rewrite Eq. (5.4b) as

$$\begin{aligned}
\langle \tilde{\phi}^{ij} | H^{(1)} | \tilde{\phi}_{ij} \rangle &\overset{sa}{=} \frac{N^2_{ij}}{4} \{ \bar{r}^{\alpha\beta}_{ij} f^{\delta}_{\beta} \bar{r}^{ij}_{\alpha\delta} - \bar{r}^{ab}_{ij} f^{d}_{b} \bar{r}^{ij}_{ad} \} - f^i_i - f^j_j \\
&= \frac{N^2_{ij}}{8} \{ \bar{r}^{\alpha\beta}_{ij} ( [f,r]^{ij}_{\alpha\beta} + (rf)^{ij}_{\alpha\beta} - [f,r]^{ji}_{\alpha\beta} - (rf)^{ji}_{\alpha\beta} ) \\
&\quad - \bar{r}^{ab}_{ij} ( [f,r]^{ij}_{ab} + (rf)^{ij}_{ab} - [f,r]^{ji}_{ab} - (rf)^{ji}_{ab} ) \} - f^i_i - f^j_j \\
&= \frac{N^2_{ij}}{8} \{ \bar{r}^{\alpha\beta}_{ij} ( -2\bar{g}^{ij}_{\alpha\beta} + 2\bar{u}^{ij}_{\alpha\beta} + \bar{r}^{\rho j}_{\alpha\beta} g^{mi}_{\rho m} + \bar{r}^{i\rho}_{\alpha\beta} g^{mj}_{\rho m} - 2 g^{m\rho}_{\beta m} \bar{r}^{ij}_{\alpha\rho} + \bar{r}^{mj}_{\alpha\beta} f^{i}_{m} + \bar{r}^{im}_{\alpha\beta} f^{j}_{m} ) \\
&\quad - \bar{r}^{ab}_{ij} ( -2\bar{g}^{ij}_{ab} + 2\bar{u}^{ij}_{ab} + \bar{r}^{\rho j}_{ab} g^{mi}_{\rho m} + \bar{r}^{i\rho}_{ab} g^{mj}_{\rho m} - 2 g^{m\rho}_{bm} \bar{r}^{ij}_{a\rho} + \bar{r}^{mj}_{ab} f^{i}_{m} + \bar{r}^{im}_{ab} f^{j}_{m} ) \} - f^i_i - f^j_j . \quad (5.8)
\end{aligned}$$

In the spirit of the standard approximation we get

$$\bar{r}^{\alpha\beta}_{ij} \bar{g}^{ij}_{\alpha\beta} - \bar{r}^{ab}_{ij} \bar{g}^{ij}_{ab} \overset{sa}{=} \bar{r}^{\kappa\lambda}_{ij} \bar{g}^{ij}_{\kappa\lambda} - \bar{r}^{pq}_{ij} \bar{r}^{ij}_{pq} = 2 - \bar{r}^{pq}_{ij} \bar{r}^{ij}_{pq}, \quad (5.9a)$$

$$\bar{r}^{\alpha\beta}_{ij} \bar{u}^{ij}_{\alpha\beta} - \bar{r}^{ab}_{ij} \bar{u}^{ij}_{ab} \overset{sa}{=} \bar{r}^{\kappa\lambda}_{ij} \bar{u}^{ij}_{\kappa\lambda} - \bar{r}^{pq}_{ij} \bar{u}^{ij}_{pq} = 3 - \bar{r}^{pq}_{ij} \bar{u}^{ij}_{pq}, \quad (5.9b)$$

where we have used that

$$r_{12} g_{12} = 1; \quad r_{12} U_{12} = -\tfrac{1}{2} \mathbf{r}_{12} (\nabla_1 - \nabla_2), \quad (5.10a)$$

$$\langle \psi(1,2) | \mathbf{r}_{12} (\nabla_1 - \nabla_2) | \psi(1,2) \rangle = -\tfrac{1}{2} \langle \psi(1,2) | [\nabla_1 - \nabla_2, \mathbf{r}_{12}] | \psi(1,2) \rangle = -3 \quad (5.10b)$$

for arbitrary $\psi$.

We further note that (see Sec. IV and Appendix A)

$$\begin{aligned}
&\bar{r}^{\alpha\beta}_{ij} \bar{r}^{\rho j}_{\alpha\beta} g^{mi}_{\rho m} - \bar{r}^{ab}_{ij} \bar{r}^{\rho j}_{ab} g^{mi}_{\rho m} \\
&\quad \overset{sa}{=} 2 [ (r^2)^{\rho j}_{ij} - (r^2)^{\rho j}_{ji} ] g^{mi}_{\rho m} - \bar{r}^{pq}_{ij} \bar{r}^{\rho j}_{pq} g^{mi}_{\rho m} \quad (5.11a)
\end{aligned}$$

while

$$\bar{r}^{\alpha\beta}_{ij} g^{m\rho}_{\beta m} \bar{r}^{ij}_{\alpha\rho} - \bar{r}^{ab}_{ij} g^{m\rho}_{bm} \bar{r}^{ij}_{a\rho} = O(l^{-7}), \quad (5.12b)$$

such that (5.12b) can be neglected in the standard approximation.

The summation of the first expression on the right-hand side of Eq. (5.11a) over the complete set $\{\rho\}$ can be done in closed form

$$\begin{aligned}
(r^2)^{\rho j}_{ij} g^{mi}_{\rho m} &= \langle ijm | r^2_{12} g_{13} | mji \rangle \\
&= \langle ijm | (r^2_1 + r^2_2 - 2\mathbf{r}_1 \mathbf{r}_2) g_{13} | mji \rangle \\
&= \langle im | r^2_1 g_{12} | mi \rangle + \langle j | r^2_1 | j \rangle \langle im | g_{12} | mi \rangle \\
&\quad - 2 \langle j | \mathbf{r}_1 | j \rangle \langle im | \mathbf{r}_1 g_{12} | mi \rangle \quad (5.13)
\end{aligned}$$

while the analogous summation of the last term in Eq. (5.11a) leads to a three-electron integral of type (4.7), which has a finite partial wave expansion. We can hence evaluate it via replacing $\rho$ by $r$, i.e., by summing over the given basis. It is probably more consistent to proceed for the first term in (5.11a) in the same way, i.e., not to use Eq. (5.13), but rather to replace $\rho$ by $r$ in both terms on the right-hand side in Eq. (5.11a).

The final expression for Eq. (5.4b) is then

$$\begin{aligned}
\langle \tilde{\phi}^{ij} | H^{(1)} | \tilde{\phi}_{ij} \rangle &\overset{sa}{=} \frac{N^2_{ij}}{4} \{ 1 + \bar{r}^{pq}_{ij} g^{ij}_{pq} - \bar{r}^{pq}_{ij} \bar{u}^{ij}_{pq} + [ (r^2)^{rj}_{ij} - (r^2)^{rj}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{rj}_{pq} ] g^{mi}_{rm} + [ (r^2)^{ir}_{ij} - (r^2)^{ir}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{ir}_{pq} ] g^{mj}_{rm} \\
&\quad + [ (r^2)^{mj}_{ij} - (r^2)^{mj}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{mj}_{pq} ] f^{i}_{m} + [ (r^2)^{im}_{ij} - (r^2)^{im}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{im}_{pq} ] f^{j}_{m} \} - f^i_i - f^j_j . \quad (5.14a)
\end{aligned}$$

For canonical spinorbits ($f^i_j = \delta^i_j \epsilon_j$) this reduces to

$$\begin{aligned}
\langle \tilde{\phi}^{ij} | H^{(1)} | \tilde{\phi}_{ij} \rangle &\overset{sa}{=} \frac{N^2_{ij}}{4} \{ 1 + \bar{r}^{pq}_{ij} \bar{g}^{ij}_{pq} - \bar{r}^{pq}_{ij} \bar{u}^{ij}_{pq} \\
&\quad + [ (r^2)^{rj}_{ij} - (r^2)^{rj}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{rj}_{pq} ] g^{mi}_{rm} \\
&\quad + [ (r^2)^{ir}_{ij} - (r^2)^{ir}_{ji} - \tfrac{1}{2} \bar{r}^{pq}_{ij} \bar{r}^{ir}_{pq} ] g^{mj}_{rm} \} . \quad (5.14b)
\end{aligned}$$

This expression is perfectly in the spirit of what we have called the standard approximation. It has nevertheless turned out that an additional simplification of Eq. (5.14b) is possible as a valid approximation, namely to ignore the terms involving the commutator $[K,r_{12}]$ altogether. In Eq. (5.14b) only the part $-r_{12}K$ is considered, because the other part $Kr_{12}$ gives only rise to truncation errors $\sim l^{-7}$, compared to $\sim l^{-5}$ for the $r_{12}K$ part. One can argue that the two

terms have opposite sign and cancel each other to some extent, such that in spite of the different $l$ behavior one should neglect both parts of $[K,r_{12}]$ rather than just one of them. If one neglects $[K,r_{12}]$ entirely, i.e., rather approximates it in the given basis, Eq. (5.14a) is replaced by

$$\begin{aligned}\langle\tilde{\phi}^{ij}|H^{(1)}|\tilde{\phi}_{ij}\rangle \overset{A}{=} \frac{N_{ij}^2}{4}\{&1+\bar{r}_{ij}^{pq}\bar{g}_{pq}^{ij}-\bar{r}_{ij}^{pq}\bar{u}_{pq}^{ij}\\&+\left[(r^2)_{ij}^{mj}-(r^2)_{ji}^{mj}-\tfrac{1}{2}\bar{r}_{ij}^{pq}\bar{r}_{pq}^{mj}\right]f_m^i\\&+\left[(r^2)_{ij}^{im}-(r^2)_{ji}^{im}\right.\\&\left.-\tfrac{1}{2}\bar{r}_{ij}^{pq}\bar{r}_{pq}^{im}\right]f_m^j\}-f_i^i-f_j^j.\end{aligned}\tag{5.14c}$$

In practical calculations[13] it has turned out that the approximation (5.14a) is generally superior to (5.14c). But the results based on Eq. (5.14c) are usually quite acceptable and obtained more easily. Since in all applications published so far[9-11] (5.14c) was implied, we shall call this the approximation $A$, and reserve the name approximation $B$ for the strict standard approximation characterized by Eq. (5.14a). This is the only place where approximations $A$ and $B$ differ. Whenever we refer to standard, this always applies to both $A$ and $B$.

The most important contribution to the difference between approximations $A$ and $B$ is that with $m=i$ or $m=j$, i.e.,

$$\left[(r^2)_{ij}^{ij}-(r^2)_{ji}^{ij}-\tfrac{1}{2}\bar{r}_{ij}^{pq}\bar{r}_{pq}^{ij}\right]g_{ri}^{ji}\tag{5.14d}$$

and the corresponding expression with $i$ and $j$ exchanged. It is surprising that such expressions arise, since matrix elements like $g_{ri}^{ji}$ usually do not occur. In the matrix element of $H^{(1)}+H^{(2)}$ these contributions cancel, as we shall see. They must, however, not be ignored if one artificially takes the matrix elements of $H^{(1)}$ and $H^{(2)}$ separately as is done in Møller–Plesset perturbation theory (see Secs. VII and VIII).

We come now to the matrix elements of $H^{(2)}$. For Eq. (3.3c) we get

$$\begin{aligned}\langle\phi|H^{(2)}|\tilde{\phi}_{ij}\rangle &\overset{\text{sa}}{=} \frac{N_{ij}}{4}\{\bar{g}_{ij}^{\kappa\lambda}\bar{r}_{\kappa\lambda}^{ij}-\bar{g}_{ij}^{pq}\bar{r}_{pq}^{ij}\}\\&=\frac{N_{ij}}{2}\{1-\tfrac{1}{2}\bar{g}_{ij}^{pq}\bar{r}_{pq}^{ij}\}.\end{aligned}\tag{5.15}$$

The result for Eq. (3.3f) is

$$\langle\phi_c^i|H^{(2)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} \frac{N_{ij}}{4}\{-\bar{g}_{cj}^{pq}\bar{r}_{pq}^{ij}\}\tag{5.16a}$$

$$\langle\phi_c^k|H^{(2)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} 0 \quad \text{for } k\neq i,j.\tag{5.16b}$$

Equations (3.3i,k) become

$$\langle\tilde{\phi}^{kl}|H^{(2)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} \frac{N_{kl}N_{ij}}{8}\bar{g}_{ij}^{kl}\{2(r^2)_{kl}^{ij}-2(r^2)_{kl}^{ji}-\bar{r}_{kl}^{pq}\bar{r}_{pq}^{ij}\};\quad \text{for } i,j\neq k,l,\tag{5.17}$$

$$\langle\phi_{cd}^{il}|H^{(2)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} 0 \text{ for } l\neq j.\tag{5.18}$$

The last term in Eq. (3.3l) and the middle term in (3.3o) need special attention.

$$\begin{aligned}\bar{R}_{il}^{\gamma\delta}\bar{g}_{\gamma j}^{\alpha l}\bar{R}_{\alpha\delta}^{ij} &= \bar{R}_{il}^{\gamma\delta}g_{\gamma j}^{\alpha l}\bar{R}_{\alpha\delta}^{ij}-\bar{R}_{il}^{\gamma\delta}g_{j\gamma}^{\alpha l}\bar{R}_{\alpha\delta}^{ij}\\&=\bar{r}_{il}^{\gamma\delta}g_{\gamma j}^{\alpha l}\bar{r}_{\alpha\delta}^{ij}-\bar{r}_{il}^{cd}g_{cj}^{\alpha l}\bar{r}_{ad}^{ij}-\bar{r}_{il}^{\gamma d}g_{\gamma j}^{\alpha l}\bar{r}_{ad}^{ij}\\&\quad+\bar{r}_{il}^{cd}g_{cj}^{\alpha l}\bar{r}_{ad}^{ij}-\bar{r}_{il}^{\gamma\delta}g_{j\gamma}^{\alpha l}\bar{r}_{\alpha\delta}^{ij}+\bar{r}_{il}^{cd}g_{jc}^{\alpha l}\bar{r}_{ad}^{ij}\\&\quad+\bar{r}_{il}^{\gamma d}g_{j\gamma}^{\alpha l}\bar{r}_{ad}^{lj}-\bar{r}_{il}^{cd}g_{jc}^{\alpha l}\bar{r}_{ad}^{ij}\\&\overset{\text{sa}}{=}\bar{r}_{il}^{\gamma\delta}g_{\gamma j}^{\alpha l}\bar{r}_{\alpha\delta}^{ij}-\bar{r}_{il}^{cd}g_{cj}^{\alpha l}\bar{r}_{ad}^{ij}-\bar{r}_{il}^{\gamma\delta}g_{j\gamma}^{\alpha l}\bar{r}_{\alpha\delta}^{ij}\\&\quad+\bar{r}_{il}^{cd}g_{jc}^{\alpha l}\bar{r}_{ad}^{ij}.\end{aligned}\tag{5.19}$$

The first two terms on the last right-hand side of (5.19) involve a Coulomb integral $g_{\gamma j}^{\alpha l}$ and are of type (4.11a), their truncation error goes as $l^{-5}$, while the last two terms involve an exchange integral $g_{j\gamma}^{\alpha l}$ and are of type (4.11c) with a truncation error $\sim l^{-7}$. We need hence only keep the first two terms. We note that [see Eq. (4.7)]

$$\begin{aligned}g_{\gamma j}^{\kappa l}r_{\kappa\delta}^{ij} &= \langle\gamma j\delta|g_{12}r_{13}|ilj\rangle\\&=\langle\gamma j\delta|r_{13}g_{12}|ilj\rangle\\&=\langle\gamma\delta j|r_{12}g_{13}|ijl\rangle\\&=r_{\gamma\delta}^{\kappa j}g_{\kappa j}^{il}\end{aligned}\tag{5.20}$$

since $g_{12}$ and $r_{13}$ commute. Hence

$$\begin{aligned}r_{il}^{\lambda\mu}g_{\lambda j}^{\kappa l}r_{\kappa\mu}^{ij} &= r_{il}^{\lambda\mu}r_{\lambda\mu}^{\kappa j}g_{\kappa j}^{il}\\&=(r^2)_{il}^{\kappa j}g_{\kappa j}^{il}\\&=\langle ilj|r_{12}^2r_{13}^{-1}|ijl\rangle,\end{aligned}\tag{5.21a}$$

$$\bar{R}_{il}^{\gamma\delta}\bar{g}_{\gamma j}^{\alpha l}\bar{R}_{\alpha\delta}^{ij} \overset{\text{sa}}{=} \{(r^2)_{il}^{\kappa j}-(r^2)_{li}^{\kappa j}-\tfrac{1}{2}\bar{r}_{il}^{pq}\bar{r}_{pq}^{\kappa j}\}g_{\kappa j}^{il}-\{(r^2)_{il}^{\kappa i}-(r^2)_{li}^{\kappa i}-\tfrac{1}{2}\bar{r}_{il}^{pq}\bar{r}_{pq}^{\kappa i}\}g_{\kappa j}^{jl},\tag{5.22a}$$

$$\begin{aligned}\langle\tilde{\phi}^{il}|H^{(2)}|\tilde{\phi}_{ij}\rangle \overset{\text{sa}}{=} \frac{N_{il}N_{ij}}{8}\{&\bar{g}_{ij}^{il}[2(r^2)_{ij}^{il}-2(r^2)_{ji}^{il}-\bar{r}_{il}^{pq}\bar{r}_{pq}^{ij}]\\&-[2(r^2)_{il}^{\kappa j}-2(r^2)_{li}^{\kappa j}-\bar{r}_{il}^{pq}\bar{r}_{pq}^{\kappa j}]g_{\kappa j}^{il}\\&+[2(r^2)_{il}^{\kappa i}-2(r^2)_{li}^{\kappa i}-\bar{r}_{il}^{pq}\bar{r}_{pq}^{i}]g_{\kappa j}^{jl}\};\quad l\neq j,\end{aligned}\tag{5.23a}$$

$$\begin{aligned}\langle\tilde{\phi}^{ij}|H^{(2)}|\tilde{\phi}_{ij}\rangle &\overset{\text{sa}}{=} \frac{N_{ij}^2}{8}\{\bar{g}_{ij}^{ij}[2(r^2)_{ij}^{ij}-2(r^2)_{ji}^{ij}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{ij}]\\&-[2(r^2)_{ij}^{\kappa j}-2(r^2)_{ji}^{\kappa j}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{\kappa j}]\\&\times[g_{\kappa j}^{ij}+g_{\kappa i}^{ji}]-[2(r^2)_{ij}^{i\kappa}-2(r^2)_{ji}^{i\kappa}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{i\kappa}]\\&\times[g_{i\kappa}^{ij}+g_{\kappa j}^{jj}]-2\bar{r}_{ij}^{ij}+\tfrac{1}{2}\bar{r}_{ij}^{pq}\bar{g}_{pq}^{rs}\bar{r}_{rs}^{ij}\}.\end{aligned}\tag{5.24a}$$

Note that

$$\frac{N_{ij}^2}{8}\bar{g}_{ij}^{ij}[2(r^2)_{ij}^{ij}-2(r^2)_{ji}^{ij}-\bar{r}_{ij}^{pq}r_{pq}^{ij}]=\bar{g}_{ij}^{ij}.\tag{5.25}$$

For the evaluation of the second and third terms in Eq. (5.24a) one can either use Eqs. (5.21a) and (5.13) for the contributions involving $r^2$, and replace the summation over $\kappa$ by a summation over $r$—or, what is more consistent, replace the summation over $\kappa$ everywhere by a summation over $r$.

Instead of exchanging the last two factors in Eq. (5.21) one could as well have exchanged the first two with the result

$$r_{il}^{\lambda\mu} g_{\lambda j}^{\kappa l} r_{\kappa\mu}^{ij} = g_{ij}^{\lambda l} r_{\lambda l}^{\kappa\mu} r_{\kappa\mu}^{ij}$$
$$= g_{ij}^{\lambda l} (r^2)_{\lambda l}^{ij}$$
$$= \langle ijl | r_{12}^{-1} r_{13}^2 | ilj \rangle, \tag{5.21b}$$

$$\overline{R}_{il}^{\gamma\delta} g_{\gamma j}^{\alpha l} \overline{R}_{\alpha\delta}^{ij} \overset{sa}{=} g_{ij}^{\lambda l} \{ (r^2)_{\lambda l}^{ij} - (r^2)_{\lambda l}^{ji} - \tfrac{1}{2} \overline{r}_{\lambda l}^{pq} \overline{r}_{pq}^{ij} \}$$
$$- g_{ij}^{\lambda l} \{ (r^2)_{\lambda l}^{ij} - (r^2)_{\lambda l}^{ji} - \tfrac{1}{2} \overline{r}_{\lambda l}^{pq} \overline{r}_{pq}^{ij} \}, \tag{5.22b}$$

$$\langle \tilde{\phi}^{il} | H^{(2)} | \tilde{\phi}_{ij} \rangle$$
$$\overset{sa}{=} \frac{N_{il} N_{ij}}{8} \{ \overline{g}_{ij}^{il} [2(r^2)_{ij}^{il} - 2(r^2)_{ji}^{il} - \overline{r}_{il}^{pq} \overline{r}_{pq}^{ij}]$$
$$- g_{ij}^{\lambda l} [2(r^2)_{\lambda l}^{ij} - 2(r^2)_{\lambda l}^{ji} - \overline{r}_{\lambda l}^{pq} \overline{r}_{pq}^{ij}]$$
$$+ g_{ij}^{\lambda l} [2(r^2)_{\lambda i}^{ij} - 2(r^2)_{\lambda i}^{ji} - \overline{r}_{\lambda i}^{pq} \overline{r}_{pq}^{ij}] \}. \tag{5.23b}$$

If one exchanges $l$ with $j$ in the second and third expressions and takes the complex conjugate one sees that the matrix defined by Eq. (5.23a) is, in fact, hermitian.

In an analogous way an alternative expression to Eq. (5.24a) is obtained:

$$\langle \tilde{\phi}^{ij} | H^{(2)} | \tilde{\phi}_{ij} \rangle$$
$$\overset{sa}{=} \overline{g}_{ij}^{ij} + \frac{N_{ij}^2}{8} \{ -2\overline{r}_{ij}^{ij} + \tfrac{1}{2} \overline{r}_{ij}^{pq} \overline{g}_{pq}^{rs} \overline{r}_{rs}^{ij}$$
$$- [g_{ij}^{\lambda j} + g_{ii}^{\lambda l}] [2(r^2)_{\lambda j}^{ij} - 2(r^2)_{\lambda j}^{ji} - \overline{r}_{\lambda j}^{pq} \overline{r}_{pq}^{ij}]$$
$$- [g_{ij}^{i\lambda} + g_{jj}^{j\lambda}] [2(r^2)_{i\lambda}^{ij} - 2(r^2)_{i\lambda}^{ji} - \overline{r}_{i\lambda}^{pq} \overline{r}_{pq}^{ij}] \}, \tag{5.24b}$$

which is the hermitian conjugate of (5.24a).

As we have mentioned after Eq. (5.14) the somewhat strange-looking terms with $g_{\kappa l}^{il}$ in Eq. (5.24a) or $g_{ii}^{\lambda l}$ in Eq. (5.24b) cancel with corresponding contributions in Eq. (5.14a) or (5.14b) if one constructs the matrix element of $H^{(1)} + H^{(2)}$.

The standard approximation for Eq. (3.3n) is obviously

$$\langle \phi_{cd}^{ij} | H^{(2)} | \tilde{\phi}_{ij} \rangle \overset{sa}{=} -\frac{N_{ij}}{4} \overline{g}_{cd}^{pq} \overline{r}_{pq}^{ij}. \tag{5.26}$$

It is not compulsory to make the standard approximation. One can, e.g., renounce on assuming (2.12b). However, all expressions then get much more lengthy, and it does not appear that one gains anything, provided that the basis is not too small.

## VI. SPINFREE FORMULATION

For a closed-shell reference state $\phi$ a spinfree formalism is recommended. We replace the excitation operators (2.2) by their spinfree counterparts:[17]

$$E_Q^P = a_{Q\alpha}^{P\alpha} + a_{Q\beta}^{P\beta}, \tag{6.1a}$$

$$E_{RS}^{PQ} = \sum_{\eta,\xi=\alpha,\beta} a_{R\eta S\xi}^{P\eta Q\xi}, \tag{6.1b}$$

where capital letters label spinfree orbitals and in Eq. (6.1) $\alpha$ and $\beta$ exceptionally refer to spin.

The normalized singlet excited configurations in analogy to Eq. (2.4) are

$$\Phi_I^A = \frac{1}{\sqrt{2}} E_I^A \phi, \tag{6.2a}$$

$$\overset{+}{\Phi}{}_{IJ}^{AB} = \tfrac{1}{2} \{ (1+\delta_{IJ})(1+\delta_{AB}) \}^{-1/2} (E_{IJ}^{AB} + E_{IJ}^{BA}) \phi$$
$$= \overset{+}{E}{}_{IJ}^{AB} \phi, \tag{6.2b}$$

$$\overset{-}{\Phi}{}_{IJ}^{AB} = \frac{1}{2\sqrt{3}} (E_{IJ}^{AB} - E_{IJ}^{BA}) \phi$$
$$= \frac{1}{\sqrt{3}} \overline{E}_{IJ}^{AB} \phi. \tag{6.2c}$$

We define the matrix elements [cf. Eq. 2.1]

$$\overset{+}{Y}{}_{RS}^{PQ} = \langle [R,S]^+ | Y | [P,Q]^+ \rangle$$
$$= \{ (1+\delta_{PQ})(1+\delta_{RS}) \}^{-1/2} (Y_{RS}^{PQ} + Y_{SR}^{PQ}), \tag{6.3a}$$

$$\overset{-}{Y}{}_{RS}^{PQ} = \langle [R,S]^- | Y | [P,Q]^- \rangle$$
$$= Y_{RS}^{PQ} - Y_{RS}^{QP}. \tag{6.3b}$$

The counterpart of Eq. (2.6) is (we keep greek lower case letters for spinfree orbitals of the complete set because greek capital letters are not unique. Note that $\alpha,\beta$ now don't mean spin functions).

$$\phi_{IJ}^+ = \frac{1}{2} \sum_{\alpha<\beta} \overset{+}{r}{}_{\alpha\beta}^{IJ} \overset{+}{E}{}_{IJ}^{\alpha\beta} \phi$$
$$= \tfrac{1}{4} (1+\delta_{\alpha\beta}) \overset{+}{r}{}_{\alpha\beta}^{IJ} \overset{+}{E}{}_{IJ}^{\alpha\beta} \phi \tag{6.4a}$$

$$\phi_{IJ}^- = \frac{1}{2\sqrt{3}} \sum_{\alpha<\beta} \overline{r}_{\alpha\beta}^{IJ} \overline{E}_{IJ}^{\alpha\beta} \phi$$
$$= \frac{1}{4\sqrt{3}} \overline{r}_{\alpha\beta}^{IJ} \overline{E}_{IJ}^{\alpha\beta} \phi. \tag{6.4b}$$

If no summation sign is given, summation over all labels independently is implied. One can multiply Eq. (6.4b) by $(1+\delta_{\alpha\beta})$ without changing anything since $\overline{r}_{\alpha\alpha}^{IJ} = 0$. The corresponding functions orthogonalized to the given basis are

$$\tilde{\phi}_{IJ}^+ = \tfrac{1}{4} N_{IJ}^+ (1+\delta_{\alpha\beta}) \overset{+}{R}{}_{\alpha\beta}^{IJ} \overset{+}{E}{}_{IJ}^{\alpha\beta} \phi, \tag{6.5a}$$

$$\tilde{\phi}_{IJ}^- = \frac{1}{4\sqrt{3}} N_{IJ}^- \overline{R}_{\alpha\beta}^{IJ} \overline{E}_{IJ}^{\alpha\beta} \phi, \tag{6.5b}$$

with $\overset{+}{R}$ and $\overline{R}$ defined in analogy to Eqs. (2.8) and (6.3).

The corresponding unnormalized functions are

$$\tilde{\tilde{\phi}}_{IJ}^+ = \tfrac{1}{4} (1+\delta_{\alpha\beta}) \overset{+}{R}{}_{\alpha\beta}^{IJ} \overset{+}{E}{}_{IJ}^{\alpha\beta} \phi, \tag{6.5c}$$

$$\tilde{\tilde{\phi}}_{IJ}^- = \tfrac{1}{4} \overline{R}_{\alpha\beta}^{IJ} \overline{E}_{IJ}^{\alpha\beta} \phi. \tag{6.5d}$$

Note that there is no factor $1/\sqrt{3}$ in Eq. (6.5d).

The spinfree Hamiltonian in particle–hole formalism is of the form Eq. (2.10a) with

$$E_o = h_I^I + 2g_{IJ}^{IJ} - g_{JI}^{IJ}, \tag{6.6a}$$

$$H^{(1)} = f_\lambda^\kappa \widetilde{E}_\kappa^\lambda; \quad f_\lambda^\kappa = h_\lambda^\kappa + 2g_{I\lambda}^{I\kappa} - g_{\lambda I}^{I\kappa}, \tag{6.6b}$$

$$H^{(2)} = \tfrac{1}{2} g_{\mu\nu}^{\kappa\lambda} \widetilde{E}_{\kappa\lambda}^{\mu\nu}. \tag{6.6c}$$

Here $\widetilde{E}$ are the spinfree excitation operators in normal order in the particle–hole sense.

For the normalization integrals we obtain

$$\langle \tilde{\phi}^{IJ}_{+} | \tilde{\phi}^{+}_{IJ} \rangle = \tfrac{1}{8}(N^{+}_{IJ})^2(1+\delta_{\alpha\beta})\overset{+}{R}{}^{\alpha\beta}_{IJ}\overset{+}{R}{}^{IJ}_{\alpha\beta}$$

$$= \tfrac{1}{4}(N^{+}_{IJ})^2 \sum_{\alpha<\beta} \overset{+}{R}{}^{\alpha\beta}_{IJ}\overset{+}{R}{}^{IJ}_{\alpha\beta},$$

$$\overset{\text{sa}}{=} \tfrac{1}{8}(N^{+}_{IJ})^2\Big[2(\overset{+}{r}{}^2)^{IJ}_{IJ} - (1+\delta_{PQ})\,\overset{+}{r}{}^{PQ}_{IJ}\overset{+}{r}{}^{IJ}_{PQ}\Big], \tag{6.7a}$$

$$(\overset{+}{r}{}^2)^{PQ}_{RS} = \{(1+\delta_{PQ})(1+\delta_{RS})\}^{-1/2}\{(r^2)^{PQ}_{RS} + (r^2)^{QP}_{RS}\}, \tag{6.7b}$$

$$\langle \tilde{\phi}^{IJ}_{-} | \tilde{\phi}^{-}_{IJ} \rangle = \tfrac{1}{8}(N^{-}_{IJ})^2\overline{R}{}^{\alpha\beta}_{IJ}\overline{R}{}^{IJ}_{\alpha\beta}$$

$$\overset{\text{sa}}{=} \tfrac{1}{8}(N^{-}_{IJ})^2[2(\overline{r}^2)^{IJ}_{IJ} - \overline{r}^{PQ}_{IJ}\overline{r}^{IJ}_{PQ}], \tag{6.7c}$$

$$(\overline{r}^2)^{PQ}_{RS} = (r^2)^{PQ}_{RS} - (r^2)^{QP}_{RS}. \tag{6.7d}$$

We get the following nonvanishing matrix elements of the one-electron operator $H^{(1)}$:

$$\langle \phi^K_C | H^{(1)} | \phi^A_I \rangle = \delta^K_I f^A_C - \delta^A_C f^K_I, \tag{6.8a}$$

$$\langle \overset{\pm}{\phi}{}^{KL}_{CD} | H^{(1)} | \overset{\pm}{\phi}{}^{AB}_{IJ} \rangle = \{(1+\delta_{AB})(1+\delta_{IJ})(1+\delta_{CD})(1+\delta_{KL})\}^{-1/2}\{(\delta^K_I\delta^L_J \pm \delta^K_J\delta^L_I)(f^A_C\delta^B_D + f^B_D\delta^A_C \pm f^A_D\delta^B_C \pm f^B_C\delta^A_D) - (\delta^A_C\delta^B_D \pm \delta^A_D\delta^B_C)(f^K_I\delta^L_J + f^L_J\delta^K_I \pm f^K_J\delta^L_I \pm f^L_I\delta^K_J)\}, \tag{6.8b}$$

$$\langle \tilde{\phi}^{KL}_{\pm} | H^{(1)} | \tilde{\phi}^{\pm}_{IJ} \rangle = \frac{N^{\pm}_{KL}N^{\pm}_{IJ}}{8}\{(1+\delta_{KL})(1+\delta_{IJ})\}^{-1/2}\Big\{2[(1+\delta_{\alpha\beta})(1+\delta_{\alpha\delta})]^{1/2}(\delta^K_I\delta^L_J \pm \delta^K_J\delta^L_I)\overset{\pm}{R}{}^{\alpha\delta}_{KL}f^{\beta}_{\delta}\overset{\pm}{R}{}^{IJ}_{\alpha\beta} - (1+\delta_{\alpha\beta})(\delta^K_I f^L_J + \delta^L_J f^K_I \pm \delta^K_J f^L_I \pm \delta^L_I f^K_J)\overset{\pm}{R}{}^{\alpha\beta}_{KL}\overset{\pm}{R}{}^{IJ}_{\alpha\beta}\Big\}. \tag{6.8c}$$

The reformulation of these expressions as well as of the analogous matrix elements of $H^{(2)}$ follows essentially the same lines as in the case of spin–orbitals. The results are somewhat lengthy and will not be given here. We shall however give the spinfree results for second- and third-order Møller–Plesset perturbation theory in the following two sections.

## VII. SECOND-ORDER MØLLER–PLESSET THEORY (MP2-R12)

Starting point is the Hylleraas functional

$$F = \langle \Psi^{(1)} | H_o - E_o | \Psi^{(1)} \rangle + 2\,\mathrm{Re}\,\langle \phi | V - E_1 | \Psi^{(1)} \rangle \tag{7.1}$$

with $\phi$ the Hartree–Fock function and with the ansatz

$$\Psi^{(1)} = \sum_{i<j}\sum_{a<b} d^{ij}_{ab}\phi^{ab}_{ij} + \sum_{i<j} c^{ij}\tilde{\phi}^{*}_{ij} \tag{7.2}$$

for the first-order function $\Psi^{(1)}$ (in spin–orbital formalism). In the standard approximation the coupling terms between $\phi^{ab}_{ij}$ and $\tilde{\phi}^{*}_{ij}$ vanish in view of Eq. (5.3), such that

$$F \overset{\text{sa}}{=} F_1 + F_2, \tag{7.3a}$$

$$F_1 = \sum_{i<j}\sum_{k<l}\sum_{a<b}\sum_{c<d} d^{cd}_{kl}d^{ij}_{ab}\langle \phi^{kl}_{cd} | H_o - E_o | \phi^{ab}_{ij} \rangle + 2\,\mathrm{Re}\sum_{i<j}\sum_{a<b} d^{ij}_{ab}\langle \phi | V | \phi^{ab}_{ij} \rangle$$

$$= \sum_{i<j}\sum_{a<b}\sum_{c<d} d^{cd}_{ij}d^{ij}_{ab}(\delta^a_c f^b_d + \delta^b_d f^a_c - \delta^a_d f^b_c - \delta^b_c f^a_d) - \sum_{i<j}\sum_{k<l}\sum_{a<b} d^{ab}_{kl}d^{ij}_{ab}(\delta^k_i f^l_j + \delta^l_j f^k_i - \delta^k_j f^l_i - \delta^l_i f^k_j) + 2\,\mathrm{Re}\sum_{i<j}\sum_{a<b} d^{ij}_{ab}\bar{g}^{ab}_{ij}, \tag{7.3b}$$

$$F_2 = \sum_{i<j}\sum_{k<l} c_{kl}c^{ij}\langle \tilde{\phi}^{*kl} | H_o - E_o | \tilde{\phi}^{*}_{ij} \rangle + 2\,\mathrm{Re}\sum_{i<j} c^{ij}\langle \phi | V | \tilde{\phi}^{*}_{ij} \rangle. \tag{7.3c}$$

One can now minimize $F_1$ with respect to the $d^{ij}_{ab}$ and $F_2$ with respect to the $c^{ij}$. If we use canonical spinorbitals ($f^p_q = \epsilon_p\delta^p_q$) the expressions (7.3) are considerably simplified [see Eq. (5.14b)]

$$F_1 = \sum_{i<j}\sum_{a<b}\{d^{ab}_{ij}d^{ij}_{ab}(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) + 2\,\mathrm{Re}\,d^{ij}_{ab}\bar{g}^{ab}_{ij}\}, \tag{7.4a}$$

$$F_2 = \sum_{i<j}\{|c^{ij}|^2\langle \tilde{\phi}^{*}_{ij} | H_o - E_o | \tilde{\phi}^{*}_{ij} \rangle + 2\,\mathrm{Re}\,c^{ij}\langle \phi | V | \tilde{\phi}^{*}_{ij} \rangle\} = \sum_{i<j}\{|c^{ij}|^2(U_{ij} + Q_{ij} - V_{ij}) + 2\,\mathrm{Re}\,c^{ij}V_{ij}\}, \tag{7.4b}$$

$$U_{ij} \overset{\text{sa}}{=} \tfrac{1}{4}[3 - \overline{r}^{pq}_{ij}\overline{u}^{ij}_{pq}], \tag{7.5a}$$

$$Q_{ij} \overset{\text{sa}}{=} \tfrac{1}{4}\{[(r^2)^{rj}_{ij} - (r^2)^{ri}_{ji} - \tfrac{1}{2}\overline{r}^{pq}_{ij}\overline{r}^{rj}_{pq}]g^{mi}_{rm} + [(r^2)^{ir}_{ij} - (r^2)^{ir}_{ji} - \tfrac{1}{2}\overline{r}^{pq}_{ij}\overline{r}^{ir}_{pq}]g^{mj}_{rm}\}, \tag{7.5b}$$

$$V_{ij} \overset{\text{sa}}{=} \tfrac{1}{4}\{2 - \bar{g}^{pq}_{ij}\overline{r}^{ij}_{pq}\}. \tag{7.5c}$$

Minimization of Eq. (7.4a) with respect to $d^{ab}_{ij}$ leads to the conventional MP2 expressions

$$d^{ab}_{ij} = \bar{g}^{ab}_{ij}(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}, \tag{7.6a}$$

$$\min(F_1) = \sum_{i<j}\sum_{a<b} |\bar{g}^{ab}_{ij}|^2(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \tag{7.6b}$$

while on minimizing $F_2$ with respect to $c^{ij}$ one gets

$$c_{ij} \overset{A}{=} -V_{ij}/(U_{ij}-V_{ij}), \tag{7.7a}$$

$$\min(F_2) \overset{A}{=} -\sum_{i<j}|V_{ij}|^2/(U_{ij}-V_{ij}), \tag{7.7b}$$

$$c_{ij} \overset{B}{=} -V_{ij}/(U_{ij}+Q_{ij}-V_{ij}), \tag{7.7c}$$

$$\min(F_2) \overset{B}{=} -\sum_{i<j}|V_{ij}|^2/(U_{ij}+Q_{ij}-V_{ij}). \tag{7.7d}$$

Equations (7.7a) and (7.7b) hold in the approximation $A$, (7.7c) and (7.7d) in the approximation $B$.

In the spinfree formalism we get (again for canonical orbitals)

$$F_1=\sum_{I<J}\sum_{A<B}\Big\{\overset{+}{d}{}^{AB}_{IJ}\overset{+}{d}{}^{IJ}_{AB}(\epsilon_A+\epsilon_B-\epsilon_I-\epsilon_J) + 2\,\mathrm{Re}\,\overset{+}{d}{}^{AB}_{IJ}\overset{+}{g}{}^{IJ}_{AB}\Big\}+\sum_{I<J}\sum_{A<B}\{\bar{d}^{AB}_{IJ}\bar{d}^{IJ}_{AB}(\epsilon_A+\epsilon_B -\epsilon_I-\epsilon_J)+2\,\mathrm{Re}\,\sqrt{3}\bar{d}^{AB}_{IJ}\bar{g}^{IJ}_{AB}\}, \tag{7.8a}$$

$$F_2=\sum_{I<J}\{|c^{IJ}_{+}|^2(U^{+}_{IJ}+Q^{+}_{IJ}-V^{+}_{IJ})+2\,\mathrm{Re}\,c^{IJ}_{+}V^{+}_{IJ}\} + 3\sum_{I<J}\{|c^{IJ}_{-}|^2(U^{-}_{IJ}+Q^{-}_{IJ}-V^{-}_{IJ})+2\,\mathrm{Re}\,c^{IJ}_{-}V^{-}_{IJ}\} \tag{7.8b}$$

with the minimum conditions

$$\overset{+}{d}{}^{AB}_{IJ}=\overset{+}{g}{}^{AB}_{IJ}(\epsilon_I+\epsilon_J-\epsilon_A-\epsilon_B)^{-1}, \tag{7.9a}$$

$$\bar{d}^{AB}_{IJ}=\sqrt{3}\,\bar{g}^{AB}_{IJ}(\epsilon_I+\epsilon_J-\epsilon_A-\epsilon_B)^{-1}, \tag{7.9b}$$

$$\min(F_1)=\sum_{I<J}\sum_{A<B}(\overset{+}{g}{}^{AB}_{IJ})^2(\epsilon_I+\epsilon_J-\epsilon_A-\epsilon_B)^{-1} + 3\sum_{I<J}\sum_{A<B}(\bar{g}^{AB}_{IJ})^2(\epsilon_I+\epsilon_J-\epsilon_A-\epsilon_B)^{-1}. \tag{7.9c}$$

Equation (7.9c) is equivalent to (7.6b). For $F_2$ one gets

$$c^{IJ}_{+} = -V^{+}_{IJ}/(U^{+}_{IJ}+Q^{+}_{IJ}-V^{+}_{IJ}), \tag{7.10a}$$

$$c^{IJ}_{-} = -V^{-}_{IJ}/(U^{-}_{IJ}+Q^{-}_{IJ}-V^{-}_{IJ}), \tag{7.10b}$$

$$\min(F_2) = -\sum_{I<J}|V^{+}_{IJ}|^2/(U^{+}_{IJ}+Q^{+}_{IJ}-V^{+}_{IJ}) - 3\sum_{I<J}|V^{-}_{IJ}|^2/(U^{-}_{IJ}+Q^{-}_{IJ}-V^{-}_{IJ}), \tag{7.10c}$$

$$V^{+}_{IJ} \overset{sa}{=} \tfrac{1}{4}\Big\{2-\overset{+}{g}{}^{PQ}_{IJ}\overset{+}{r}{}^{IJ}_{PQ}(1+\delta_{PQ})\Big\}, \tag{7.11a}$$

$$V^{-}_{IJ} \overset{sa}{=} \tfrac{1}{4}\{2-\bar{g}^{PQ}_{IJ}\bar{r}^{IJ}_{PQ}\}, \tag{7.11b}$$

$$U^{+}_{IJ} \overset{sa}{=} \tfrac{1}{4}\Big\{3-\overset{+}{r}{}^{PQ}_{IJ}\overset{+}{u}{}^{IJ}_{PQ}(1+\delta_{PQ})\Big\}, \tag{7.11c}$$

$$Q^{+}_{IJ} \overset{sa}{=} \tfrac{1}{4}\Big\{\Big[(\overset{+}{r}{}^2)^{RJ}_{IJ}-\tfrac{1}{2}\overset{+}{r}{}^{PQ}_{IJ}\overset{+}{r}{}^{RJ}_{PQ}(1+\delta_{PQ})\Big]g^{MI}_{RM} \times(1+\delta_{RJ})^{1/2}+\Big[(\overset{+}{r}{}^2)^{IR}_{IJ}-\tfrac{1}{2}\overset{+}{r}{}^{PQ}_{IJ}\overset{+}{r}{}^{IR}_{PQ} \times(1+\delta_{PQ})\Big]g^{MJ}_{RM}(1+\delta_{IR})^{1/2}\Big\}(1+\delta_{IJ})^{-1/2}, \tag{7.11d}$$

$$U^{-}_{IJ} \overset{sa}{=} \tfrac{1}{4}\{3-\bar{r}^{PQ}_{IJ}\bar{u}^{IJ}_{PQ}\}, \tag{7.11e}$$

$$Q^{-}_{IJ} \overset{sa}{=} \tfrac{1}{4}\Big\{\Big[(\bar{r}^2)^{RJ}_{IJ}-\tfrac{1}{2}\bar{r}^{PQ}_{IJ}\bar{r}^{RJ}_{PQ}\Big]g^{MI}_{RM} + \Big[(\bar{r}^2)^{IR}_{IJ}-\tfrac{1}{2}\bar{r}^{PQ}_{IJ}\bar{r}^{IR}_{PQ}\Big]g^{MJ}_{RM}\Big\}. \tag{7.11f}$$

In conventional MP2 the results from the spinorbital formalism and the spinfree formalism are identical. In MP2-R12 this is not longer the case (except in the limit of a complete basis). The cusp-relation requires[20] that for high enough $l$ $c_{ij}$ approaches 1 for a natural parity singlet state, but $\frac{1}{2}$ for a triplet state and $\frac{1}{3}$ for an unnatural parity singlet state. For spinorbital pairs that are mixtures of singlet and triplet states a "compromise" $c_{ij}$ is obtained that does not guarantee an $(l+\frac{1}{2})^{-8}$ convergence of the remaining terms. The use of spin-adapted pairs is hence compulsory.

In conventional MP2 it also does not matter whether ones uses canonical or localized orbitals. This is again different in MP2-R12. (For details see paper III of this series.[13])

## VIII. THIRD-ORDER MØLLER–PLESSET THEORY

The third-order energy $E^{(3)}$ of the MP expansion can be expressed in terms of the first-order wave function $\Psi^{(1)}$ given by Eq. (7.2). It is convenient to decompose $E^{(3)}$ into three parts $E_a$, $E_b$, and $E_c$ corresponding to the traditional expression, a mixed term and an $r_{12}$ term, respectively.

$$E^{(3)}=E_a+E_b+E_c. \tag{8.1}$$

In the spinorbital formalism we get

$$E_a=\sum_{i<j}\sum_{k<l}\sum_{a<b}\sum_{c<d}d^{cd}_{kl}\langle\phi^{kl}_{cd}|H^{(2)}|\phi^{ab}_{ij}\rangle d^{ij}_{ab}, \tag{8.2a}$$

$$E_b=2\,\mathrm{Re}\sum_{i<j}\sum_{k<l}\sum_{c<d}d^{cd}_{kl}\langle\phi^{kl}_{cd}|H^{(2)}|\tilde{\phi}_{ij}\rangle c^{ij}, \tag{8.2b}$$

$$E_c=\sum_{i<j}\sum_{k<l}c_{kl}\langle\tilde{\phi}^{kl}|H^{(2)}|\tilde{\phi}_{ij}\rangle c^{ij}. \tag{8.2c}$$

The matrix elements needed in Eqs. (8.2) have been derived in Secs. III and V.

It is recommended to decouple $E_a$, $E_b$, and $E_c$ into particle–particle ($pp$), particle–hole ($ph$), and hole–hole ($hh$) contributions, according to whether matrix elements, $g^{ab}_{cd}$ ($pp$), $g^{al}_{cj}$ or $g^{al}_{jc}$ ($ph$), or finally $g^{kl}_{ij}$ ($hh$) are involved.

$$E_a=E^{pp}_a+E^{ph}_a+E^{hh}_a, \tag{8.3a}$$

$$E_b=E^{pp}_b, \tag{8.3b}$$

$$E_c=E^{pp}_c+E^{ph}_c+E^{hh}_c, \tag{8.3c}$$

$$E^{pp}_a=\sum_{i<j}\sum_{a<b}\sum_{c<d}d^{cd}_{ij}\bar{g}^{ab}_{cd}d^{ij}_{ah}, \tag{8.4a}$$

$$E^{ph}_a=\sum_{i,j,k}\sum_{a,b,c}d^{ij}_{ab}\bar{g}^{ak}_{ic}d^{cb}_{kj}, \tag{8.4b}$$

$$E^{hh}_a=\sum_{i<j}\sum_{k<l}\sum_{a<b}d^{ab}_{ij}\bar{g}^{ij}_{kl}d^{kl}_{ab}, \tag{8.4c}$$

$$E^{pp}_b \overset{sa}{=} -\tfrac{1}{2}\mathrm{Re}\sum_{i<j}c^{ij}d^{cd}_{ij}\bar{g}^{pq}_{cd}\bar{r}^{ij}_{pq}, \tag{8.5}$$

$$E^{pp}_c \overset{sa}{=} \tfrac{1}{16}\sum_{i<j}(\bar{r}^{pq}_{ij}\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs}-4\bar{r}^{ij}_{ij})|c^{ij}|^2, \tag{8.6a}$$

$$E_c^{ph}\overset{sa}{=} -\tfrac{1}{8}\sum_{i,j,l}\{[2(r^2)_{il}^{rj}-2(r^2)_{li}^{rj}-\bar{r}_{il}^{pq}\bar{r}_{pq}^{rj}]g_{rj}^{il}$$
$$-[2(r^2)_{il}^{ri}-2(r^2)_{li}^{ri}-\bar{r}_{il}^{pq}\bar{r}_{pq}^{ri}]g_{rj}^{jl}\}c_{ij}c^{il}, \quad (8.6b)$$

$$E_c^{hh}\overset{sa}{=}\tfrac{1}{8}\sum_{i<j}\sum_{k<l}c_{ij}\bar{g}_{kl}^{ij}c^{kl}\{2(r^2)_{kl}^{ij}-2(r^2)_{kl}^{ji}-\bar{r}_{kl}^{pq}\bar{r}_{pq}^{ij}\}. \quad (8.6c)$$

The corresponding expressions in the spinfree formalism are

$$E_a^{pp}=\sum_{I<J}\sum_{A<B}\sum_{C<D}\overset{+}{d}{}_{IJ}^{CD}\overset{+}{g}{}_{CD}^{AB}\overset{+}{d}{}_{AB}^{IJ}+\sum_{I<J}\sum_{A<B}\sum_{C<D}\bar{d}_{IJ}^{CD}\bar{g}_{CD}^{AB}\bar{d}_{AB}^{IJ} \quad (8.7a)$$

$$E_a^{ph}=\frac{1}{4}\sum_{I,J,K}\sum_{A,B,C}\Big\{-\overset{+}{d}{}_{AB}^{IJ}\Big[\overset{+}{g}{}_{CI}^{AK}+3\bar{g}_{CI}^{AK}\Big]\overset{+}{d}{}_{KJ}^{CB}$$
$$+\bar{d}_{AB}^{IJ}\Big[\overset{+}{g}{}_{CI}^{AK}-5\bar{g}_{CI}^{AK}\Big]\bar{d}_{KJ}^{CB}+\sqrt{3}\overset{+}{d}{}_{AB}^{IJ}\Big[\overset{+}{g}{}_{CI}^{AK}-\bar{g}_{CI}^{AK}\Big]$$
$$\times\bar{d}_{KJ}^{CB}+\sqrt{3}\bar{d}_{AB}^{IJ}\Big[\overset{+}{g}{}_{CI}^{AK}-\bar{g}_{CI}^{AK}\Big]\overset{+}{d}{}_{KJ}^{CB}\Big\}\{(1+\delta_{IJ})$$
$$\times(1+\delta_{AB})(1+\delta_{KJ})(1+\delta_{CB})\}^{1/2}, \quad (8.7b)$$

$$E_a^{hh}=\sum_{I<J}\sum_{K<L}\sum_{A<B}\overset{+}{d}{}_{KL}^{AB}\overset{+}{g}{}_{IJ}^{KL}\overset{+}{d}{}_{AB}^{IJ}$$
$$+\sum_{I<J}\sum_{K<L}\sum_{A<B}\bar{d}_{KL}^{AB}\bar{g}_{IJ}^{KL}\bar{d}_{AB}^{IJ} \quad (8.7c)$$

$$E_b^{pp}=-\frac{1}{2}\mathrm{Re}\sum_{I<J}\sum_{C<D}\overset{+}{d}{}_{IJ}^{CD}\overset{+}{g}{}_{CD}^{PQ}\overset{+}{r}{}_{PQ}^{IJ}(1+\delta_{PQ})c_+^{IJ}$$
$$-\frac{\sqrt{3}}{2}\mathrm{Re}\sum_{I<J}\sum_{C<D}\bar{d}_{IJ}^{CD}\bar{g}_{CD}^{PQ}\bar{r}_{PQ}^{IJ}c_-^{IJ} \quad (8.8)$$

$$E_c^{pp}=\frac{1}{16}\sum_{I<J}c_{IJ}^{+}c_+^{IJ}\Big[\overset{+}{r}{}_{IJ}^{PQ}\overset{+}{g}{}_{PQ}^{RS}\overset{+}{r}{}_{RS}^{IJ}(1+\delta_{PQ})(1+\delta_{RS})$$
$$-4\overset{+}{r}{}_{IJ}^{IJ}\Big]+\frac{3}{16}\sum_{I<J}c_{IJ}^{-}c_-^{IJ}[\bar{r}_{IJ}^{PQ}\bar{g}_{PQ}^{RS}\bar{r}_{RS}^{IJ}-4\bar{r}_{IJ}^{IJ}], \quad (8.9a)$$

$$E_c^{ph}=-\frac{1}{8}\sum_{I,J,L}c_{IJ}^{+}c_+^{IL}\Big\{\Big[2(\overset{+}{r}{}^2)_{IL}^{RJ}-\overset{+}{r}{}_{IL}^{PQ}\overset{+}{r}{}_{PQ}^{RJ}(1+\delta_{PQ})\Big]g_{RJ}^{IL}(1+\delta_{RJ})^{1/2}+\Big[2(\overset{+}{r}{}^2)_{IL}^{RI}-\overset{+}{r}{}_{IL}^{PQ}\overset{+}{r}{}_{PQ}^{RI}(1+\delta_{PQ})\Big]$$
$$\times g_{RJ}^{JL}(1+\delta_{RI})^{1/2}\}(1+\delta_{IL})^{1/2}-\frac{3}{8}\sum_{I,J,L}c_{IJ}^{-}c_-^{IL}\{[2(\bar{r}^2)_{IL}^{RJ}-\bar{r}_{IL}^{PQ}\bar{r}_{PQ}^{RJ}]g_{RJ}^{IL}-[2(\bar{r}^2)_{IL}^{RI}-\bar{r}_{IL}^{PQ}\bar{r}_{PQ}^{RI}]g_{RJ}^{JL}\}, \quad (8.9b)$$

$$E_c^{hh}=\frac{1}{8}\sum_{I<J}\sum_{K<L}c_{KL}^{+}c_+^{IJ}\overset{+}{g}{}_{IJ}^{KL}\Big\{2(\overset{+}{r}{}^2)_{KL}^{IJ}$$
$$-\overset{+}{r}{}_{KL}^{PQ}\overset{+}{r}{}_{PQ}^{IJ}(1+\delta_{PQ})\Big\}+\frac{3}{8}\sum_{I<J}c_{KL}^{-}c_-^{IJ}$$
$$\times\{2(\bar{r}^2)_{KL}^{IJ}-\bar{r}_{KL}^{PQ}\bar{r}_{PQ}^{IL}\}. \quad (8.9c)$$

An analysis of the various contributions to $E^{(3)}$ in terms of their partial wave increments in the atomic case leads to the following result.

$E_b^{pp}$ as given by Eq. (8.5) or Eq. (8.8) goes as $(l+\frac{1}{2})^{-4}$, $E_c^{pp}$ as given by Eq. (8.6a) or Eq. (8.9a) as $(l+\frac{1}{2})^{-5}$,[1,20] finally $E_c^{ph}$ [Eqs. (8.6b)–(8.9b)] and $E_c^{hh}$ [Eqs. (8.6c)–(8.9c)] as $(l+\frac{1}{2})^{-6}$. Obviously $E_b^{pp}$ is the most important correction to the conventional $E^{(3)}$, followed by $E_c^{pp}$.

One sees that the contributions to $E_c^{ph}$ have a very similar structure as those neglected in approximation $A$ for $E^{(2)}$. In fact the contribution of $E^{(2)}$ neglected in approximation $A$ is

$$\sum_{i<j}|c_{ij}|^2G_{ij}=\frac{1}{8}\sum_{i<j}|c_{ij}|^2\{[2(\bar{r}^2)_{ij}^{rj}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{rj}]g_{rm}^{mi}$$
$$+[2(\bar{r}^2)_{ij}^{ir}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{ir}]g_{rm}^{mj}\}. \quad (8.10)$$

Compare this with the contributions with $j=l$ to $E_c^{ph}$

$$-\frac{1}{8}\sum_{i,j}|c_{ij}|^2\{[2(\bar{r}^2)_{ij}^{ir}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{rj}]g_{rj}^{ij}$$
$$+[2(\bar{r}^2)_{ij}^{ir}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{ir}]g_{rj}^{ij}\} \quad (8.11)$$

or rather the corresponding expression symmetrized between $i$ and $j$:

$$-\frac{1}{8}\sum_{i<j}|c_{ij}|^2\{[2(\bar{r}^2)_{ij}^{rj}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{rj}](g_{rj}^{ij}+g_{ri}^{ji})$$
$$+[2(\bar{r}^2)_{ij}^{ir}-\bar{r}_{ij}^{pq}\bar{r}_{pq}^{ir}](g_{rj}^{ji}+g_{ri}^{ij})\}. \quad (8.12)$$

One sees that in $E^{(2)}+E^{(3)}$ the terms containing $g_{ri}^{ij}$ or $g_{rj}^{ji}$ cancel and those with $g_{rj}^{ij}$ in Eq. (8.12) combine with corresponding contributions in Eq. (8.10) to terms with $\bar{g}_{rj}^{ij}$.

If one has evaluated $E^{(2)}$ by means of approximation $A$ one should make an approximation of the same kind for $E^{(3)}$, i.e., one should exclude $J=L$ in Eq. (8.9b).

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## APPENDIX: THE PARTIAL WAVE EXPANSION OF TWO-, THREE-, AND FOUR-ELECTRON INTEGRALS IN THE ATOMIC CASE

Let $f(r_{12})$ be some function of $r_{12}$ with the partial wave expansion

$$f(r_{12})=\sum_{l=0}^{\infty}\{f_l\}=\sum_{l=0}^{\infty}f_l(r_1,r_2)P_l(\cos\vartheta_{12}) \quad (A1)$$

and $g(r_{12})$ be another function of $r_{12}$ with an analogous expansion. A two-electron integral

$$A = \langle \varphi(1,2) | f(r_{12}) g(r_{12}) | \varphi(1,2) \rangle \tag{A2}$$

can then be expanded in partial waves as well. The situation is simplest if $\varphi(1,2)$ only depends on $r_1$ and $r_2$ and on no angles. We shall here only consider this case. The generalization to arbitrary $\varphi(1,2)$ is straightforward, but somewhat tedious. However, the essential results are hardly changed.[20]

Under the assumption $\varphi(1,2) = \varphi(r_1,r_2)$ only "diagonal" terms contribute to Eq. (A2), i.e.,

$$A = \sum_{l=0}^{\infty} A_l; \quad A_l = \langle \varphi(1,2) | f_l g_l P_l^2(\cos \vartheta_{12}) | \varphi(1,2) \rangle. \tag{A3}$$

The angular integration in $A_l$ can then be carried out

$$A_l = 8\pi^2 (l+\tfrac{1}{2})^{-1} \int |\varphi(r_1,r_2)|^2 f_l(r_1,r_2) g_l(r_1,r_2) \times r_1^2 r_2^2 \, dr_1 \, dr_2. \tag{A4}$$

We first consider the case

$$f_l = g_l = (r_{12}^{-1})_l = r_<^l r_>^{-l-1}. \tag{A5}$$

The factor

$$f_l g_l r_<^2 r_>^2 = r_<^{2l+2} r_>^{-2l} \tag{A6}$$

in Eq. (A4) is then strongly peaked around $r_< = r_>$. In order to get the leading term in an expansion of powers of $(l+\frac{1}{2})^{-1}$ we can replace $\varphi(r_<,r_>)$ by $\varphi(r_>,r_>)$ and integrate over $r_<$ from 0 to $r_>$. Then only an integral over $r_>$ remains. We rename the integration variable as $r$.

$$\begin{aligned} A_l &= 16\pi^2 (l+\tfrac{1}{2})^{-1} (2l+3)^{-1} \int_0^\infty |\varphi(r,r)|^2 r^3 \, dr \\ &\quad + O([l+\tfrac{1}{2}]^{-3}) \\ &= 8\pi^2 (l+\tfrac{1}{2})^{-2} \int_0^\infty |\varphi(r,r)|^2 r^3 \, dr \\ &\quad + O([l+\tfrac{1}{2}]^{-4}). \end{aligned} \tag{A7}$$

For the case $f(r_{12}) = r_{12}^{-1}$ and $g(r_{12}) = r_{12}$,

$$g_l = (r_{12})_l = \frac{1}{2l+3} \frac{r_<^{l+2}}{r_>^{l+1}} - \frac{1}{2l-1} \frac{r_<^l}{r_>^{l-1}}, \tag{A8}$$

one gets by the same procedure[20]

$$\begin{aligned} A_l &= 16\pi^2 (l+\tfrac{1}{2})^{-1} \left\{ \frac{1}{(2l+3)(2l+5)} - \frac{1}{(2l-1)(2l+3)} \right\} \\ &\quad \times \int |\varphi(r,r)|^2 r^5 \, dr + O([l+\tfrac{1}{2}]^{-5}) \\ &= -12\pi^2 (l+\tfrac{1}{2})^{-4} \int_0^\infty |\varphi(r,r)|^2 r^5 \, dr \\ &\quad + O([l+\tfrac{1}{2}]^{-6}). \end{aligned} \tag{A9}$$

For $f(r_{12}) = g(r_{12}) = r_{12}$ one obtains

$$\begin{aligned} A_l &= 16\pi^2 (l+\tfrac{1}{2})^{-1} \left\{ \frac{1}{(2l+3)^2(2l+7)} - \frac{2}{(2l+5)(2l+3)(2l-1)} + \frac{1}{(2l-1)^2(2l-3)} \right\} \\ &\quad \times \int_0^\infty |\varphi(r,r)|^2 r^7 \, dr + O\left[(l+\tfrac{1}{2})^{-7}\right] \\ &= 80\pi^2 (l+\tfrac{1}{2})^{-6} \\ &\quad \times \int_0^\infty |\varphi(r,r)|^2 r^7 \, dr + O([l+\tfrac{1}{2}]^{-8}). \end{aligned} \tag{A10}$$

One sees that both the angular and the radial integration lead to a factor $\sim (l+\frac{1}{2})^{-1}$ each. If one replaces $r_{12}^{-1}$ by $r_{12}$, two more factors $\sim (l+\frac{1}{2})^{-1}$ arise, one that is explicit in Eq. (A8), the other because there are two terms with opposite sign such that the leading terms in $(l+\frac{1}{2})^{-1}$ cancel.

For two-electron integrals with three factors

$$B = \langle \varphi(1,2) | f(r_{12}) g(r_{12}) h(r_{12}) | \varphi(1,2) \rangle \tag{A11}$$

the partial wave expansion is, *a priori*, a threefold sum, which for $\varphi = \varphi(r_1,r_2)$ reduces to a double sum. We define the partial wave increment $B_l$ as

$$\begin{aligned} B_l &= \langle \varphi | \{f_l\} g(r_{12}) \{h_l\} | \varphi \rangle \\ &\quad + \sum_{k=0}^{l-1} \langle \varphi | \{f_l\} g(r_{12}) \{h_k\} | \varphi \rangle \\ &\quad + \sum_{k=0}^{l-1} \langle \varphi | \{f_k\} g(r_{12}) \{h_l\} | \varphi \rangle \end{aligned} \tag{A12}$$

in each term in the sum Eq. (A12) only those partial waves of $g$ contribute which are compatible with the triangular inequality. For the special case $f = h = r_{12}$, $g = r_{12}^{-1}$, the sum Eq. (A12) has been evaluated in closed form with the result[1,20]

$$B_l = -\frac{192}{5} \pi (l+\tfrac{1}{2})^{-5} \times \int_0^\infty |\varphi(r,r)|^2 r^6 \, dr + O([l+\tfrac{1}{2}]^{-6}). \tag{A13}$$

The dependence on the fifth power of $(l+\frac{1}{2})^{-1}$ can be rationalized if one realizes that each term in the sum Eq. (A12) goes as $(l+\frac{1}{2})^{-6}$, while the number of terms is of the order $l$.

We now come to three-electron integrals, first to those with two factors

$$D = \langle \varphi(1,2,3) | f(r_{12}) g(r_{23}) | \varphi(1,2,3) \rangle. \tag{A14}$$

If one expands $f$ and $g$ one gets

$$D = \langle \varphi(1,2,3) | \sum_{k,l} f_k(r_1,r_2) g_l(r_2,r_3) P_k(\cos \vartheta_{12}) \times P_l(\cos \vartheta_{23}) | \varphi(1,2,3) \rangle. \tag{A15}$$

Noting that

$$P_k(\cos\vartheta_{12})P_l(\cos\vartheta_{23}) = \frac{(4\pi)^2}{(2k+1)(2l+1)}\sum_{m,m'} Y_k^m(1) \times Y_k^{m*}(2)Y_l^{m'}(2)Y_l^{m'*}(3) \quad \text{(A16)}$$

one sees that integration over $d^3\mathbf{r}_1$ gives a nonvanishing contribution only for a finite number of $k$ values, so does integration over $d^3\mathbf{r}_3$ for a finite number of $l$ values. The expansion Eq. (A15) hence breaks off after a finite number of terms. For the special case that $\varphi(1,2,3)$ is built up from $s$ orbitals only, $k$ and $l$ must be equal to 0 and $D$ reduces to a single term. Then evaluation of $D$ by means of a completeness insertion only requires a basis of $s$ AO's. The highest angular momentum necessary for a completeness relation is easily found. (See Appendix A of paper II of this series.[12])

Three-electron integrals with three factors are of the following types:

$$E = \langle\varphi(1,2,3)|f(r_{12})g(r_{12})h(r_{13})|\varphi(1,2,3)\rangle, \quad \text{(A17)}$$

$$F = \langle\varphi(1,2,3)|f(r_{12})g(r_{23})h(r_{13})|\varphi(1,2,3)\rangle, \quad \text{(A18)}$$

and we also need to consider four-electron integrals

$$G = \langle\varphi(1,2,3,4)|f(r_{12})g(r_{23})h(r_{34})|\varphi(1,2,3,4)\rangle, \quad \text{(A19)}$$

$$H = \langle\varphi(1,2,3,4)|f(r_{12})g(r_{13})h(r_{14})|\varphi(1,2,3,4)\rangle. \quad \text{(A20)}$$

The four-electron integrals Eqs. (A19) and (A20) have finite partial wave expansions like Eq. (A14); the three-electron integral (A17) has a finite expansion as far as the partial wave expansion of $h$ is concerned, with respect to $f$ and $g$ the integral (A17) behaves as Eq. (A4), i.e., for $f=r_{12}$, $g=r_{12}^{-1}$ the partial wave expansion goes as $(l+\frac{1}{2})^{-4}$ or for $f=g=r_{12}$ as $(l+\frac{1}{2})^{-6}$. Fortunately this partial wave expansion need not be made. One simply rewrites

$$f(r_{12})g(r_{12}) = k(r_{12}) \quad \text{(A21)}$$

[with for the examples just given $k(r_{12})=1$ and $k(r_{12})=r_{12}^2$, respectively] and can then reduce Eq. (A17) to (A14). Equation (A18) is, in a way, the least pleasant integral since it does not break off after a finite number of terms. Fortunately its partial-wave expansion is very rapidly convergent. The angular factor in the expansion of Eq. (A18) is

$$P_j(\cos\vartheta_{12})P_k(\cos\vartheta_{23})P_l(\cos\vartheta_{13}) = \frac{(4\pi)^3}{(2j+1)(2k+1)(2l+1)} \times \sum_{m,m',m''} Y_j^m(1)Y_j^{m*}(2)Y_k^{m'}(2) \times Y_k^{m'*}(3)Y_l^{m''*}(1)Y_l^{m''}(3). \quad \text{(A22)}$$

Consider again the simplest case that $\varphi$ is built up from $s$ AOs only. The integration over the angular variables of the first particle yields a nonvanishing result only if $j=l$, $m=m''$. Similarly one finds $j=k$, $m=m'$ and finally

$$j=k=l, \quad m=m'=m''. \quad \text{(A23)}$$

The integral (A18) hence reduces to a single sum (summation over $m$ yields a factor $2l+1$)

$$F = (4\pi)^3\sum_{l=0}^{\infty}(2l+1)^{-2}\int\varphi^2(r_1,r_2,r_3)f_l(r_1,r_2) \times g_l(r_2,r_3)h_l(r_3,r_1)r_1^2r_2^2r_3^2\,dr_1\,dr_2\,dr_3. \quad \text{(A24)}$$

Let us now study the result of the radial integration in Eq. (A24). To simplify the argument we first take $f=g=h=r_{12}^{-1}$. If we define

$$r_> = \max(r_1,r_2,r_3), \quad r_< = \min(r_1,r_2,r_3), \quad r_< < r_0 < r_>, \quad \text{(A25)}$$

we see that

$$fgh = \frac{r_<^{2l}}{r_0 r_>^{2l+2}}; \quad fghr_1^2r_2^2r_3 = \frac{r_<^{2l+2}r_0}{r_>^{2l}}. \quad \text{(A26)}$$

For large $l$ this product strongly peaks at $r_< = r_0 = r_>$, and we can replace $\varphi(r_1,r_2,r_3)$ by $\varphi(r,r,r)$ where $r=r_>$. We can then integrate over $r_<$ from 0 to $r_0$ with the result

$$\frac{1}{2l+3}\frac{r_0^{2l+4}}{r_>^{2l}}, \quad \text{(A27)}$$

then over $r_0$ from 0 to $r_>$ with the result

$$\frac{r_>^5}{(2l+3)(2l+5)}, \quad \text{(A28)}$$

such that

$$F_l = 24\pi^3(l+\tfrac{1}{2})^{-4}\int\varphi(r,r,r)r^5\,dr + O([l+\tfrac{1}{2}]^{-6}). \quad \text{(A29)}$$

In Eq. (A29) a factor 6 accounts for the six possible orderings of $r_1,r_2,r_3$.

We now come to the integral in which we are actually interested, namely Eq. (A18) with $f=h=r_{12}$, $g=r_{12}^{-1}$.

For the product $fgh$ we get three different expressions depending on whether $r_1=r_>$, $r_1=r_0$, or $r_1=r_<$.

$$fgh = \frac{1}{(2l+3)^2}\frac{r_0r_<^{2l+2}}{r_>^{2l+2}} - \frac{1}{(2l+3)(2l-1)} \times\left[\frac{r_<^{2l+2}}{r_0r_>^{2l}} + \frac{r_0r_<^{2l}}{r_>^{2l}}\right] + \frac{1}{(2l-1)^2}\frac{r_<^{2l}}{r_0r_>^{2l-2}}, \quad \text{for } r_1=r_>, \quad \text{(A31a)}$$

$$fgh = \frac{1}{(2l+3)^2}\frac{r_0r_<^{2l+2}}{r_>^{2l+2}} - \frac{1}{(2l+3)(2l-1)} \times\left[\frac{r_<^{2l+2}}{r_0r_>^{2l}} + \frac{r_0^3r_<^{2l}}{r_>^{2l+2}}\right] + \frac{1}{(2l-1)^2}\frac{r_0r_<^{2l}}{r_>^{2l}}, \quad \text{for } r_1=r_0 \quad \text{(A31b)}$$

$$fgh = \frac{1}{(2l+3)^2}\frac{r_<^{2l+4}}{r_0r_>^{2l+2}} - \frac{1}{(2l+3)(2l-1)} \times\left[\frac{r_<^{2l+2}}{r_0r_>^{2l}} + \frac{r_0r_<^{2l+2}}{r_>^{2l+2}}\right] + \frac{1}{(2l-1)^2}\frac{r_0r_<^{2l}}{r_>^{2l}}, \quad \text{for } r_1=r_<. \quad \text{(A31c)}$$

We multiply Eqs. (A31) by $r_>^2r_0^2r_<^2$ and integrate first over $r_<$ then over $r_0$. The result of the first integration is

$$\frac{1}{(2l+3)^2(2l+5)}\frac{r_0^{2l+8}}{r_>^{2l}}-\frac{1}{(2l+3)(2l-1)}\times\left[\frac{1}{2l+5}\frac{r_0^{2l+6}}{r_>^{2l-2}}+\frac{1}{2l+3}\frac{r_0^{2l+6}}{r_>^{2l-2}}\right]+\frac{1}{(2l-1)^2(2l+3)}\frac{r_0^{2l+4}}{r_>^{2l-4}} \tag{A32a}$$

$$\frac{1}{(2l+3)^2(2l+5)}\frac{r_0^{2l+8}}{r_>^{2l}}-\frac{1}{(2l+3)(2l-1)}\times\left[\frac{1}{2l+5}\frac{r_0^{2l+6}}{r_>^{2l-2}}+\frac{1}{2l+3}\frac{r_0^{2l+8}}{r_>^{2l}}\right]+\frac{1}{(2l-1)^2(2l+3)}\frac{r_0^{2l+6}}{r_>^{2l-2}} \tag{A32b}$$

$$\frac{1}{(2l+3)^2(2l+7)}\frac{r_0^{2l+8}}{r_>^{2l}}-\frac{1}{(2l+3)(2l-1)}\times\left[\frac{1}{2l+5}\frac{r_0^{2l+6}}{r_>^{2l-2}}+\frac{1}{2l+5}\frac{r_0^{2l+8}}{r_>^{2l}}\right]+\frac{1}{(2l-1)^2(2l+3)}\frac{r_0^{2l+6}}{r_>^{2l-2}} \tag{A32c}$$

while the second integration yields

$$\left\{\frac{1}{(2l+3)^2(2l+5)(2l+9)}-\frac{1}{(2l+3)(2l-1)(2l+7)}\times\left[\frac{1}{2l+5}+\frac{1}{2l+3}\right]+\frac{1}{(2l-1)^2(2l+3)(2l+5)}\right\}r_>^9, \tag{A33a}$$

$$\left\{\frac{1}{(2l+3)^2(2l+5)(2l+9)}-\frac{1}{(2l+3)(2l-1)}\times\left[\frac{1}{(2l+5)(2l+7)}+\frac{1}{(2l+3)(2l+9)}\right]+\frac{1}{(2l-1)^2(2l+3)(2l+7)}\right\}r_>^9, \tag{A33b}$$

$$\left\{\frac{1}{(2l+3)^2(2l+7)(2l+9)}-\frac{1}{(2l+3)(2l-1)(2l+5)}\times\left[\frac{1}{2l+7}+\frac{1}{2l+9}\right]+\frac{1}{(2l-1)^2(2l+3)(2l+7)}\right\}r_>^9. \tag{A33c}$$

The final result of the radial integration is hence

$$\frac{35}{8}(l+\tfrac{1}{2})^{-6}\int|\varphi(r,r,r)|^2r^9\,dr. \tag{A34}$$

Together with the $(l+\frac{1}{2})^{-2}$ from the angular integration we get a final $(l+\frac{1}{2})^{-8}$ dependence of the partial wave increments.

$$F_l=70\pi^3(l+\tfrac{1}{2})^{-8}\int|\varphi(r,r,r)|^2r^9\,dr+O([l+\tfrac{1}{2}]^{-10}). \tag{A35}$$

This corresponds to an asymptotic truncation error $\Delta E_l$ of the energy for a partial wave expansion truncated at some $l$

$$\Delta E_l=10\pi^3(l+1)^{-7}\int\varphi\,|(r,r,r)|^2r^9\,dr+O[(l+1)^{-9}]. \tag{A36}$$

The results for the numerical example for $\varphi$ a product of three equal normalized 1$s$ functions with

$$\frac{\alpha^9}{\pi^3}\int e^{-6\alpha r}r^9\,dr=35/(8\cdot729\pi^3\alpha) \tag{A37}$$

are illustrated in Table I. Both the rapid convergence and the

TABLE I. Partial-wave expansion of the integral $\alpha\int|\varphi(1)\varphi(2)\varphi(3)|^2r_{12}r_{23}^{-1}r_{13}d^3r_1d^3r_2d^3r_3$ with $\varphi=(\alpha^{3/2}/\sqrt{\pi})e^{-\alpha r}$.

| $l$ | Exact[a] | Asympt.[b] | Trunc. Err[c] | Asympt. Trunc. Err[d] | Corr. Trunc. Err[e] |
|---|---|---|---|---|---|
| 0 | 2.847 608 025 | | 0.035 958 570 | 0.060 137 174 | −0.024 055 147 |
| 1 | 0.035 608 715 | 0.016 391 492 | 0.000 349 855 | 0.000 468 857 | −0.000 119 002 |
| 2 | 0.000 326 493 | 0.000 275 314 | 0.000 023 363 | 0.000 027 441 | −0.000 004 078 |
| 3 | 0.000 020 045 | 0.000 018 655 | 0.000 003 317 | 0.000 003 663 | −0.000 000 346 |
| 4 | 0.000 002 599 | 0.000 002 498 | 0.000 000 719 | 0.000 000 768 | −0.000 000 049 |
| 5 | 0.000 000 514 | 0.000 000 502 | 0.000 000 204 | 0.000 000 214 | −0.000 000 010 |
| 6 | 0.000 000 134 | 0.000 000 132 | 0.000 000 070 | 0.000 000 073 | −0.000 000 003 |
| 7 | 0.000 000 042 | 0.000 000 042 | 0.000 000 028 | 0.000 000 029 | −0.000 000 001 |
| 8 | 0.000 000 016 | 0.000 000 015 | 0.000 000 012 | 0.000 000 013 | −0.000 000 001 |
| 9 | 0.000 000 006 | 0.000 000 006 | 0.000 000 006 | 0.000 000 006 | −0.000 000 000 |
| 10 | 0.000 000 003 | 0.000 000 003 | 0.000 000 003 | 0.000 000 003 | −0.000 000 000 |
| Σ | 2.883 566 593 | | | | |
| f | 2.883 566 595 | | | | |

[a] Exact partial-wave contributions.
[b] From the asymptotic formula (A35).
[c] Error of the expansion truncated at $l$.
[d] Asymptotic truncation error from (A36).
[e] Error of the expression truncated at $l$, but corrected for the asymptotic part of the remainder.
[f] Closed expression derived by R. N. Hill (Ref. 14) and computed with his program.

TABLE II. Partial wave expansion of the integral $\alpha\int|\varphi(1)\varphi(2)\varphi(3)|^2 r_{12}r_{12}r_{13}^{-1}d^3r_1 d^3r_2 d^3r_3$ with $\varphi=(\alpha^{3/2}/\sqrt{\pi})e^{-\alpha r}$.

| $l$ | Exact[a] | Asympt.[b] | Trunc. Err[c] | Asympt. Trunc. Err[d] | Corr. Trunc. Err[e] |
|---|---|---|---|---|---|
| 0 | 2.994 876 280 | | 0.192 623 719 | 0.153 490 441 | + 0.039 133 278 |
| 1 | 0.187 819 019 | 0.067 375 776 | 0.004 804 700 | 0.004 796 576 | + 0.000 008 124 |
| 2 | 0.004 177 684 | 0.003 143 484 | 0.000 627 016 | 0.000 631 648 | − 0.000 004 632 |
| 3 | 0.000 478 047 | 0.000 417 487 | 0.000 148 969 | 0.000 149 893 | − 0.000 000 924 |
| 4 | 0.000 100 080 | 0.000 092 422 | 0.000 048 889 | 0.000 049 117 | − 0.000 000 228 |
| 5 | 0.000 029 220 | 0.000 027 725 | 0.000 019 669 | 0.000 019 739 | − 0.000 000 070 |
| 6 | 0.000 010 562 | 0.000 010 176 | 0.000 009 107 | 0.000 009 132 | − 0.000 000 025 |
| 7 | 0.000 004 434 | 0.000 004 312 | 0.000 004 673 | 0.000 004 684 | − 0.000 000 010 |
| 8 | 0.000 002 079 | 0.000 002 035 | 0.000 002 594 | 0.000 002 599 | − 0.000 000 005 |
| 9 | 0.000 001 062 | 0.000 001 044 | 0.000 001 532 | 0.000 001 535 | − 0.000 000 003 |
| 10 | 0.000 000 581 | 0.000 000 572 | 0.000 000 952 | 0.000 000 953 | − 0.000 000 001 |
| Σ | 3.187 499 048 | | | | |
| f | 3.187 500 000 | | | | |

[a] Exact partial-wave contributions.
[b] From the asymptotic formula (A41).
[c] Error of the expansion truncated at $l$.
[d] Asymptotic truncation error from (A42).
[e] Error of the expression truncated at $l$, but corrected for the asymptotic part of the remainder.
[f] From Eq. (A37).

validity of the asymptotic formulas (A35) and (A36) are obvious. If one truncates at $l=4$ and corrects for the truncation error by means of (A37) one gets the integral accurate to eight significant figures, for a truncation at $l=2$ to six significant figures. Without the correction (A37) one loses one significant figure.

Less rapidly convergent is the partial wave expansion of the integral $E$ (A17) with $f=g=r_{12}$, $h=1/r_{12}$.

This integral is relatively easily evaluated in closed form

$$N^6\int r_{12}^2\frac{1}{r_{13}}e^{-2\alpha(r_1+r_2+r_3)}r_1^2r_2^2r_3^2\,dr_1\,dr_2\,dr_3=\frac{51}{16\alpha}. \tag{A38}$$

The evaluation of the exact partial wave increments (which are given in Table II) is rather tedious and is not outlined here. For the asymptotic formula like (A35) we rewrite the partial wave increment of the integral.

$$\frac{1}{2l+1}\int|\phi(1,2)|^2|\varphi(3)|^2(r_{12}^3_k\frac{1}{r_{13}}r_1^2r_2^2r_3^2\,dr_1\,d_2\,dr_3$$
$$=\frac{1}{2l+1}\int g(1,2)(r_{12})_k^2r_1^2r_2^2\,dr_1\,dr_2 \tag{A39a}$$

$$g(1,2)=4\pi|\phi(1,2)|^2\int dr_3|\varphi(r_3)|^2\frac{1}{r_{13}}r_3^2$$
$$=4\pi|\phi(1,2)|^2\left\{r_1^{-1}\int_0^{r_1}dr_3|\varphi(3)|^2r_3^2\right.$$
$$\left.+\int_{r_1}^{\infty}dr_3|\varphi(3)|^2r_3\right\}. \tag{A39b}$$

We then use Eq. (A10) to get

$$\int g(1,2)(r_{12})_k^2r_1^2r_2^2\,dr_1\,dr_2=5(l+\tfrac{1}{2})^{-5}\int_0^{\infty}g(r,r)r^7\,dr$$
$$+O(l^{-6}). \tag{A40}$$

The final result for a product of three 1$s$ Slater functions is

$$E_l=\frac{25\cdot17\cdot337}{256\cdot729\alpha}\cdot(l+\tfrac{1}{2})^{-6} \tag{A41}$$

while the truncation error of the energy is given by

$$\Delta E_l=\frac{5\cdot17\cdot337}{256\cdot729\alpha}(l+1)^{-5}. \tag{A42}$$

The correction for the asymptotic truncation error by means of (A42) is now even more effective than in the case of Table I; one gains two to three significant figures by this correction. The corrected truncation error appears to go as $(l+1)^{-9}$ in Table I and as $(l+1)^{-7}$ in Table II.

Tables I and II illustrate that it is justified to evaluate integrals like that in Table II—which go as $(l+\frac{1}{2})^{-6}$—exactly, but to use truncated partial wave expansions for integrals like that in Table I—which go as $(l+\frac{1}{2})^{-8}$. To use a truncated PWE for both types of integrals would be less balanced.

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