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Coupled cluster theory that takes care of the correlation cusp by inclusion of linear terms in the interelectronic coordinates

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CC-R12—a combination of coupled cluster theory and the R12 method, is presented in which the correlation cusp is treated via inclusion of terms explicitly dependent on the interelectronic distance r_{ij} into the exponential expansion of the wave function. A diagrammatic derivation of the CC-R12 equations within the so-called "standard approximation B" is given at the level of singles, doubles and triples (CCSDT-R12). MBPT(4)-R12 is derived as a byproduct of CCSDT-R12. Fifth order noniterative corrections are also discussed.

I. INTRODUCTION

Traditional quantum chemical methods, even those accounting for a large part of electron correlation, suffer from a rather slow convergence to the exact solution of the Schrödinger equation on extension of the basis. Within a CI (configuration interaction) or CC (coupled cluster) approach in a finite one-electron basis, one is unable to describe the correlation cusp correctly,[1–4] i.e., the cusp relation[5]

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

is not satisfied. That the explicit inclusion of the interelectronic coordinates r_{ij} into the wave function is a powerful means to speed up the convergence has been known since Hylleraas suggested such an approach in his study of the He atom,[6] and has been definitely confirmed in the calculation by Kołos and Wolniewicz of the potential curve of the hydrogen molecule.[7] Explicit inclusion of terms linear in r_{ij} (and/or odd powers of r_{ij}) as it is done in "Hylleraas CI"[8,9] leads to the appearance of "difficult" three- and four-electron integrals, which makes the computation prohibitive except for very small molecules. An alternative approach with explicit r_{ij} dependence as well, the so-called Gaussian geminal method,[10] has the advantage that no difficult integrals arise, but the correlation cusp is not strictly taken care of and a sophisticated optimization of nonlinear parameters is needed. Although random tempering of Gaussian geminals leads to significant savings in CPU timings,[11] the method still remains computationally very demanding.

More recently, one of us together with Klopper has suggested a theory in which explicit r_{ij}-dependent terms in the wave function expansion are present, but where the evaluation of difficult integrals is avoided.[2,3,12] In this R12 method the linear r_{ij}-dependent terms are considered in the final wave function via inclusion of pair functions like

$$|\tilde{\phi}_{ij}\rangle=\tfrac{1}{2}\,\bar{R}^{ij}_{\alpha\beta}\tilde{a}^{\alpha\beta}_{ij}|0\rangle=\tfrac{1}{2}\,(\bar{r}^{ij}_{\alpha\beta}\tilde{a}^{\alpha\beta}_{ij}-\bar{r}^{ij}_{ab}\tilde{a}^{ab}_{ij})|0\rangle, \tag{2a}$$

$$\bar{r}^{ij}_{ab}=\langle ab|r_{12}|ij\rangle-\langle ab|r_{12}|ji\rangle \tag{2b}$$

into its CI expansion.

We use the labels $i,j,...$ for occupied, $a,b,...$ for virtual, and $p,q,...$ for arbitrary molecular orbitals expandable in the actual basis, while $\alpha,\beta,...$ and $\kappa,\lambda,...$ correspond to virtual and arbitrary orbitals, respectively, within the complete basis. Operators and matrix elements are written in a tensor notation,[13,14] i.e., $\tilde{a}^{p}_{q}\;=\;:a^{\dagger}_{p}a_{q}:$, $\tilde{a}^{pq}_{rs}\;=\;:a^{\dagger}_{p}a^{\dagger}_{q}a_{r}a_{s}:$ where double dots (as well as the tilde on $\tilde{a}^{p}_{q}$, etc.) mark normal products in the particle hole sense; $X^{q}_{p}=\langle p|X|q\rangle$ and $\bar{Y}^{pq}_{rs}=Y^{pq}_{rs}-Y^{qp}_{rs}=\langle rs|Y|pq\rangle-\langle rs|Y|qp\rangle$. The Einstein summation convention will be implied throughout this paper, i.e., all expressions are summed over all indices that do not match the target ones on the left-hand side of equations.

The ansatz Eq. (2) has, among others, two very attractive features:

(i) One clearly sees that the additional functions are orthogonal to the reference function $|0\rangle$.
(ii) It transparently shows that the improvement with respect to the conventional approach consists in a partial implicit replacement of the given basis by a complete basis. It may hence be termed a correction for basis incompleteness.[3,12] In fact Eq. (2) corresponds to a wave function in which the pair $i(1)j(2)$ of occupied spin-orbitals is replaced by $r_{12}i(1)j(2)$, with the part of this function describable in the given basis projected out.

After the description of some pilot calculations,[3] a general theory has been published,[12] within which all necessary matrix elements have been derived for CI-R12, CEPA-R12, MBPT(2)-R12, and MBPT(3)-R12, based on a single Slater determinant reference function, i.e., for CI, CEPA, etc., improved by inclusion of linear r_{ij} terms. In order to avoid difficult integrals the "standard approximation" (as variants A and B, *vide infra*) have played an important role. The various R12 approaches have rather successfully been applied to many-electron systems, both atoms and molecules.[15]

A minor drawback of the use of pair functions of the type (2) is that the results are not invariant with respect to a unitary transformation among the occupied MOs.[12] One then takes the best advantage of the R12 method in using localized MOs. Fortunately, Klopper has found a modification[16] which is invariant with respect to this kind of unitary trans-

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formation and has applied it in the context of MBPT(2). We follow the same procedure.

The main virtue of the R12 method is that one reaches the *basis set limit* within one kind of approach, say MBPT(2) rather easily. In order to approach the exact solution of the Schrödinger equation one must as well proceed in a hierarchy of approximations that converge sufficiently fast towards full CI in the given basis. The best such hierarchy available at present is that of coupled-cluster (CC) methods. A combination of the R12 method with the coupled-cluster approach should therefore be rather powerful. Quite recently we have proposed this combination, where the r_{ij}-dependent terms have been included via the exponential cluster operator. Pilot calculations on Be_2 at the CCSD[T]-R12 level of theory clearly demonstrated the power of the suggested CC-R12 method.[17] (In Ref. 17 we have suggested the shorthand notation CCSD[T] instead of the original name CCSD+T(CCSD)[18]). In the present paper we give a detailed derivation of the CC-R12 equations up to CCSDT-R12, while MBPT(4)-R12 (a byproduct of CCSDT-R12), as well as various so-called noniterative corrections are also discussed. A diagrammatic technique is used for the derivation of the explicit equations. Orthogonally spin adapted equations are presented in addition to the spin-free ones.

II. THE CC-R12 ANSATZ

A common feature of all coupled-cluster methods is the exponential ansatz for the wave function

$$|\Psi\rangle = e^{S}|0\rangle, \tag{3}$$

where in conventional approaches $S=T$ is usually a global excitation operator consisting of single, double, triple, etc., excitation operators

$$T=T_1+T_2+T_3+\cdots=t_a^i\tilde{a}_i^a+\frac{1}{4}\,t_{ab}^{ij}\tilde{a}_{ij}^{ab}+\frac{1}{36}\,t_{abc}^{ijk}\tilde{a}_{ijk}^{abc}+\cdots\,. \tag{4}$$

We here use the tensor notation introduced previously.[13,14] (Note that in the literature one finds other definitions for the t amplitudes, e.g., t_i^a—in the meaning of our t_a^i—that would not be consistent with our tensor notation).

Via Eq. (3), the final wave function is expanded in the basis of all possible configuration state functions generated by e^T. We want to extend this basis by functions similar to those of Eq. (2); but at the same time preserve the cluster structure of the final wave function. In other words we search for an operator $\mathscr{R}$ which takes care of the correlation cusp, and which can be plugged into S in addition to T, i.e., we choose $S=T+\mathscr{R}$.

The operator $\mathscr{R}$ is essentially of the same form as T_2 given by Eq. (4), but with the summation over the given basis a,b replaced by the orthogonal complement to the latter within the complete basis α,β. This implies that $\mathscr{R}$ commutes with T. Let the operator $\mathscr{R}$ be defined as

$$\mathscr{R}=\frac{1}{4}\,c_{kl}^{ij}\tilde{\mathscr{R}}_{ij}^{kl}, \tag{5}$$

$$\tilde{\mathscr{R}}_{ij}^{kl}=\frac{1}{2}\,\bar{R}_{\alpha\beta}^{kl}\tilde{a}_{ij}^{\alpha\beta}, \tag{6a}$$

$$\bar{R}_{\alpha\beta}^{kl}\tilde{a}_{ij}^{\alpha\beta}=\bar{r}_{\alpha\beta}^{kl}\tilde{a}_{ij}^{\alpha\beta}-\bar{r}_{ab}^{kl}\tilde{a}_{ij}^{ab}\,. \tag{6b}$$

Irrespectively of the associated amplitude c_{ij}^{kl}, $\mathscr{R}$ is just a generalization of the operator in Eq. (2). If in Eq. (6b) we restrict the operators $\tilde{\mathscr{R}}_{kl}^{ij}$ to diagonal ones, i.e., $\tilde{\mathscr{R}}_{kl}^{kl}$, then also the coefficients would be diagonal $c_{kl}^{kl}=c_{kl}$, the action of $\mathscr{R}$ on $|0\rangle$ would mean that the spin–orbital pair (kl) is multiplied by $c_{kl}r_{12}$ and then orthogonalized to (kl), which leads formally to a sum of doubly excited determinants, involving a complete set (hence the labels α,β). This would correspond to the use of the r_{12} functions taken in previous papers.[3,12,15] The form actually chosen in Eq. (6) means that (kl) is replaced by (ij) multiplied by $c_{kl}^{ij}r_{12}$ [and orthogonalized to (kl)]. This is in the spirit of the orbital-invariant r_{12} approach introduced in the context of second order perturbation theory.[16] Then the results do not depend on whether one uses canonical or localized orbitals. Otherwise it would be imperative to use localized ones.[15] Unlike for the original ansatz Eq. (2), now also such configuration states will be created via the operator e^S, which result from the action of $\mathscr{R}$ on excited determinants (in a conventional sense).

Let us point out that we have changed one convention with respect to previous papers.[12–17] While previously we have regarded $c_{kl}=c_{kl}^{kl}$ as the coefficient of the term $\frac{1}{2}r_{12}[k,l]$, we now regard it as the coefficient of $r_{12}[k,l]$. This means that in the limit of a complete basis, c_{kl} now gets the value 1/2 for (natural parity) singlet pairs and 1/4 for triplet pairs, while formerly it got the respective values 1 or 1/2. This transfer of the factor 1/2 from r_{12} to c_{kl} implies a redefinition of some intermediates. To avoid confusion, all new intermediates are symbolized by caligraphical letters, while the old ones were represented by ordinary latin letters. Only for the coefficients c_{ij}^{kl} we have not introduced a new symbol.

Usually the new intermediates (like $\mathscr{V}_{ij}^{kl}$, $\mathscr{X}_{ij}^{kl}$, etc.) differ from the old ones (like V_{ij}^{kl},X_{ij}^{kl}) by a factor 2^{k-l} if they contain k $\mathscr{R}_{ij}^{kl}$ factors and l c_{ij}^{kl} factors. The operator $\mathscr{R}$ defined by Eq. (5) is the same in the old and the new convention, while $\tilde{\mathscr{R}}_{ij}^{kl}$ is the counterpart of the former $\mathscr{R}_{ij}^{kl}$.[17]

We have to solve the Schrödinger equation

$$H_Ne^S|0\rangle=\Delta Ee^S|0\rangle \tag{7}$$

with ΔE the correlation energy and H_N the normal product form of the Hamiltonian in the particle–hole picture, with the reference Slater determinant $|0\rangle$ as the new "physical vacuum."

$$H_N=F_N+W_N, \tag{8a}$$

$$F_N=f_\kappa^\lambda\tilde{a}_\lambda^\kappa;\quad W_N=\tfrac{1}{4}\bar{g}_{\kappa\lambda}^{\mu\nu}\tilde{a}_{\nu\mu}^{\kappa\lambda}, \tag{8b}$$

$$f_\kappa^\lambda=h_\kappa^\lambda+\bar{g}_{\kappa i}^{\lambda i}. \tag{8c}$$

The choice of $\mathscr{R}$ [Eq. (5)] guarantees the orthogonality of the resulting functions to $|0\rangle$ and consequently the intermediate normalization ($\langle 0|\Psi\rangle=1$).

The traditional way of deriving the CC equations, has been[19] to project Eq. (7) from the left successively by $\langle 0|$,

$\langle 0|\tilde{a}^i_a$, $\langle 0|\tilde{a}^{ij}_{ab}$, etc., or by $\langle 0|e^{-S}$, $\langle 0|\tilde{a}^i_a e^{-S}$, etc. This is equivalent to[20,21] projecting Eq. (7) from the left by $\langle 0|(1+S^\dagger)$ or $\langle 0|(1+S^\dagger)e^{-S}$ and subsequent differentiation with respect to the amplitudes of $S^\dagger$. (The insertion of e^{-S} makes the linked structure of the expressions transparent, but does not affect the results). For our ansatz with $S=T+\mathscr{R}$ the projection with $\langle 0|(1+S)^\dagger$ and subsequent differentiation with respect to the parameters t^i_a, etc., and c^{ij}_{kl} is particularly straightforward. We get

$$\langle 0|(H_N e^S)_C|0\rangle = \Delta E, \tag{9a}$$

$$\langle 0|\tilde{a}^{ij\ldots}_{ab\ldots}(H_N e^S)_C|0\rangle = 0, \tag{9b}$$

$$\langle 0|(\tilde{\mathscr{R}}^{kl}_{ij})^\dagger (H_N e^S)_C|0\rangle = 0. \tag{9c}$$

The subscript C in Eq. (9) means connected.

In the following it will be convenient to treat the operator $\mathscr{R}$ formally as a doubly contracted product of two operators, namely (we use parentheses for single contractions and double parentheses for double contractions, see Appendix A)

$$\mathscr{R} = ((\mathscr{C}\mathscr{R}_0)), \tag{10a}$$

$$\mathscr{C} = \tfrac{1}{4} c^{ij}_{kl} \tilde{a}^{kl}_{ij} \tag{10b}$$

$$\mathscr{R}_0 = \tfrac{1}{4} \bar{R}^{kl}_{\alpha\beta} \tilde{a}^{\alpha\beta}_{kl} \tag{10c}$$

One must keep in mind that $\mathscr{C}$ is never present without a $\mathscr{R}$ and that $\mathscr{C}$ and $\mathscr{R}$ are always contracted over two hole lines (k,l). By this trick one is able to treat the coefficients t^{ij}_{ab} and c^{ij}_{kl} on the same footing. In the diagrammatic formulation both t^{ij}_{ab} and c^{ij}_{kl} are represented by a vertex, and so is $\bar{R}^{kl}_{\alpha\beta}$.

III. DIAGRAMMATIC REPRESENTATION OF THE CCSDT-R12 EQUATIONS AND THEIR SPIN–ORBITAL FORMULATION

The elementary constituents of the diagrams are fermion lines (usually vertical, carrying arrows) and vertices (horizontal). Fermion lines with downgoing arrows symbolize holes (labels $i,j,k,\ldots$), upgoing lines with a single arrow particles lines within the given basis $(a,b,c,\ldots)$, up-going lines with double arrows particle lines corresponding to a complete basis (α,β,γ). Horizontal fermion lines mean either particles or holes, with a single arrow corresponding to the given basis (labels $p,q,r,\ldots$), with a double arrow to the complete basis (labels $\kappa,\lambda,\mu,\ldots$).

A broken-line vertex symbolizes the electron interaction $(\bar{g}^{rs}_{pq})$ when it carries fermion lines on both sides, or the Fock operator (f^p_q) if it has fermion lines only on one side. A double solid line represents matrix elements of the T operator $(t^i_a, t^{ij}_{ab}$, etc.) or the $\mathscr{C}$ operator (c^{ij}_{kl}), i.e., essentially the coefficients in terms of which the S operator is defined. A triple line represents matrix elements of the R operator $(\bar{R}^{ij}_{\alpha\beta})$. Note that all vertices are antisymmetrized.

Fermion lines may be external, i.e., be open ended and enter or leave the diagram, or internal (contracted) i.e., start at one vertex and end on another one. Scalar quantities (expectation values) are described by diagrams without external lines, one-particle operators contain one ingoing and one outgoing fermion line, two particle operators two ingoing, and two outgoing fermion lines, etc.

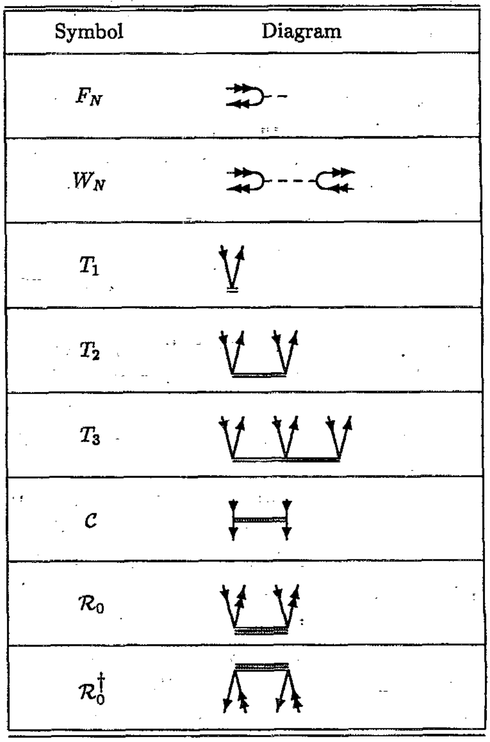

FIG. 1. The diagrammatic definition of operators. Horizontal lines can be either hole or particle ones.

Note that our use of double arrows (for the complete set) differs from that of, e.g., Lindgren[22] where double arrows indicate active (partially occupied) orbitals. These are not present in the closed-shell states that we are interested in here.

The basis operators are presented in Fig. 1.

Since the number of hole labels is finite, no discrimination between single and double down-going arrows for hole lines is necessary. Only lines of the same type can contract. Contraction of a particle line with double arrow and one with single arrow leads to an internal line with a single arrow. From a wealth of $\mathscr{R}$-containing diagrams that can be constructed in principle, we may *a priori* exclude those diagrams in which no lines with double arrows occur. Their contributions vanish due to the definition of $\mathscr{R}$.

We restrict our consideration to $T=T_1+T_2+T_3$, i.e., up to full CCSDT-R12. Then, in addition to the conventional CC scheme, the following terms survive in the expansion of Eqs. (9):

$$\Delta E = \mathrm{CC}^{(0)}_{\mathrm{conv}} + \langle 0|(W_N \mathscr{R})_C|0\rangle, \tag{11a}$$

$$0 = \mathrm{CC}^{(1)}_{\mathrm{conv}} + \langle 0|\tilde{a}^i_a (W_N \mathscr{R} + W_N \mathscr{R} T_1)_C|0\rangle, \tag{11b}$$

$$0 = \mathrm{CC}^{(2)}_{\mathrm{conv}} + \langle 0|\tilde{a}^{ij}_{ab}(W_N \mathscr{R} + W_N \mathscr{R} T_1 + W_N \mathscr{R} T_2 + \tfrac{1}{2} W_N \mathscr{R} T_1 T_1 + \tfrac{1}{2} W_N \mathscr{R}\mathscr{R})_C|0\rangle, \tag{11c}$$

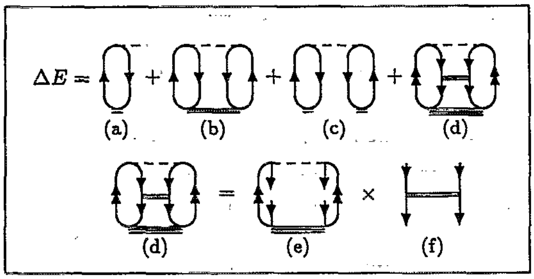

FIG. 2. CC-R12 energy diagrams.

$$0=\mathrm{CC}^{(3)}_{\mathrm{conv}}+\langle 0|\tilde{a}^{ijk}_{abc}(W_N\mathscr{R}+W_N\mathscr{R}T_1+W_N\mathscr{R}T_2+\tfrac{1}{2}W_N\mathscr{R}\mathscr{R}$$
$$+\tfrac{1}{2}W_N\mathscr{R}T_1T_1+W_N\mathscr{R}T_3+W_N\mathscr{R}T_2T_1+\tfrac{1}{6}W_N\mathscr{R}T_1^3$$
$$+\tfrac{1}{2}W_N\mathscr{R}\mathscr{R}T_1)_C|0, \tag{11d}$$
$$0=\langle 0|\mathscr{R}_0^{\dagger}\tilde{a}^{ij}_{kl}(F_N\mathscr{R})_C|0\rangle+\langle 0|\mathscr{R}_0^{\dagger}\tilde{a}^{ij}_{kl}(W_N+W_NT_2+W_N\mathscr{R}$$
$$+W_NT_1+W_N\mathscr{R}T_2+\tfrac{1}{2}W_N\mathscr{R}^2+W_N\mathscr{R}T_1$$
$$+\tfrac{1}{2}W_N\mathscr{R}T_1^2)_C|0\rangle. \tag{11e}$$

Here $\mathrm{CC}^{(k)}_{\mathrm{conv}}$ stands for the conventional contributions, that can be found in the literature,[17,19,23–25] and that we do not want to give in detail here—except diagrammatically for Eqs. (11a) and (11b). A compact formulation of the CC-R12 equations to be given later (on Fig. 9 in terms of some intermediates as defined in Fig. 8) will also include the conventional part.

We can now start to represent Eq. (11) by diagrams. The diagrammatic representation of Eq. (11a) is seen on Fig. 2. The first three diagrams (a) to (c) represent the conventional result and the fourth one (d) the r_{12} correction. The analytic expression corresponding to the first line of Fig. 2 is

$$\Delta E=f^a_i t^i_a+\tfrac{1}{4}\bar{g}^{ab}_{ij}t^{ij}_{ab}+\tfrac{1}{2}\bar{g}^{ab}_{ij}t^i_a t^j_b+\tfrac{1}{8}\bar{g}^{\alpha\beta}_{ij}c^{ij}_{kl}\bar{R}^{kl}_{\alpha\beta} \tag{12}$$

while the second line on Fig. 2 illustrates that the diagram (d) is a contracted product of the "amplitudeless" diagram (e)

$$\mathscr{V}^{kl}_{ij}=\tfrac{1}{2}\bar{g}^{\alpha\beta}_{ij}\bar{R}^{kl}_{\alpha\beta} \tag{13}$$

and the diagram (f) representing the $\mathscr{C}$ operator defined by Eq. (10b).

The conventional way to solve the CC equations (11) is by iteration. One rewrites, e.g., Eq. (9b) for T_1 and T_2, that they become

$$D^{ia}_{ia}t^i_a=(f^i_i-f^a_a)t^i_a=f_1(f^s_r,\bar{g}^{pt}_{rs},t^j_b,t^{jk}_{bc},\ldots c^{jk}_{lm}), \tag{14a}$$
$$D^{ijab}_{ijab}t^{ij}_{ab}=(f^i_i+f^j_j-f^a_a-f^b_b)t^{ij}_{ab}$$
$$=f_2(f^s_r,\bar{g}^{pt}_{rs},t^k_c,t^{kl}_{cd},\ldots c^{kl}_{mn}). \tag{14b}$$

One sets all variables t^j_b, etc., on the right-hand side (r.h.s.) of Eq. (14) equal to 0 and solves for t^i_a, t^{ij}_{ab}, etc. Then one inserts the variables from the previous iteration on the r.h.s. of Eq. (14) to get new t^i_a, etc., and one proceeds until self-consistency.

It is, of course, not compulsory to choose this iterative procedure. However, if one does so, as is usually the case, one will have to evaluate ΔE in every iteration. It is therefore recommended to evaluate the $\mathscr{V}^{kl}_{ij}$, as given by Eq. (13), and to store them before entering the iterations. We shall encounter more such expressions that are calculated prior to the iteration procedure.

The equations for T_1 are represented diagrammatically on Fig. 3. In addition to the part known from conventional CC theory there are r_{12}-containing diagrams. The parts of the diagrams d3.2 and d3.3 on Fig. 3, with identical lines entering and leaving the f vertex, just represent the l.h.s. of Eq. (14a). If the Brillouin theorem holds, the diagrams d3.1 and d3.5 vanish and for canonic Hartree–Fock orbitals also the off-diagonal parts of d3.2 and d3.3 (with different lines at the f vertex) vanish.

One recognizes on Fig. 3, like on Fig. 2, that the r_{12} terms (involving triple vertices) contain a part that is independent of the coefficients t^i_a, etc., and c^{kl}_{ij}, and that can be evaluated and stored before the iteration start.

The full graphical representations of Eq. (11c) and (11d) become very lengthy. We shall later give them in a compact form.

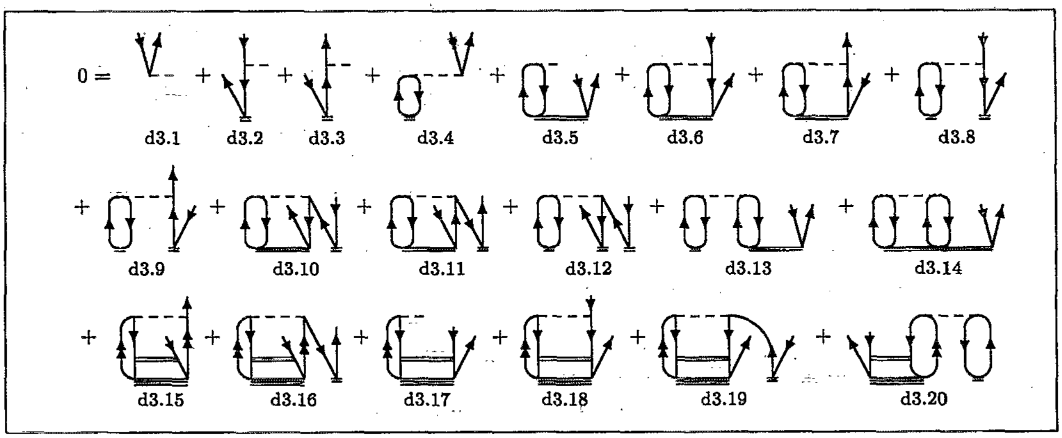

FIG. 3. The diagrammatic form of T_1 equation.

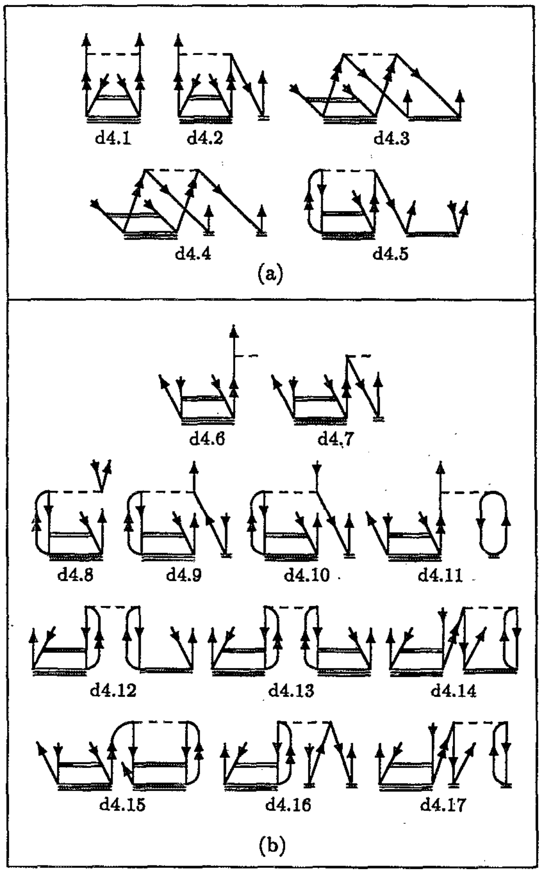

FIG. 4. $\mathscr{R}$ containing T_2 diagrams within the CC-R12 method. (a) Diagrams that remain in the standard approximation. (b) Diagrams that vanish due to the standard approximation.

The R12 diagrams that complement the equations for the T_2 and T_3 amplitudes are collected in Figs. 4 and 5, while the diagrams arising in Eq. (11e) are in Fig. 6. Before coming to the more compact form of Eq. (11b) to (11e) (which will be found on Fig. 9 in terms of some intermediates defined on Fig. 8) some general considerations are necessary.

All the diagrams in Figs. 4 and 5 contain summations over complete sets of virtual orbitals. Closed expressions for these sums are possible, but they involve matrix elements of 2-particle, 3-particle or even 4-particle operators, as discussed elsewhere.[12] Such an access is prohibitive. Fortunately, what we have termed the standard approximation appears to work nicely. (At this point we need not yet discriminate between the standard approximations A and B[12]).

The standard approximation is based on the assumption that the one-particle basis is large enough such that

(a) the Hartree–Fock equations can be assumed to be satisfied exactly;
(b) sums over a complete one-particle basis in expressions like $A^{ij}_{\kappa\mu}B^{l\mu}_{nm}$ are well approximated by a sum in the given basis, i.e., (for A and B spherically symmetric two-particle operators like r_{12}^{-1})

$$A^{k\mu}_{ij}B^{nm}_{l\mu}=A^{kp}_{ij}B^{nm}_{lp}. \tag{15}$$

For i,j,k,l,m,n referring to occupied MOs, the sum over μ corresponding to a complete basis can be replaced by the sum over p corresponding to the given basis. For details see Appendix C.

The justification of the standard approximation lies in the fact that it becomes exact for atoms provided the basis is saturated up to some finite l value depending on the case (e.g., $l=1$ for He, Be or $l=3$ for Ne, Ar[12]). There is further evidence[26] that for molecules the truncation error at this level decreases exponentially with l. The unsaturation error within a given l goes as $\exp(-\alpha\sqrt{n})$ with the basis dimension n,[27] at least for an even-tempered basis.

Equation (15) is valid also for a more general case (see Appendix C). This implies that all diagrams with only one double-arrowed line between two vertices will vanish (i.e., the diagrams d3.17 to d3.20, those from Figs. 4(b) and 5(b) as well as diagrams d6.22–d6.34).

The standard approximation allows us further to write[12] (see also the Appendix A)

$$\bar{A}^{\alpha\beta}_{pq}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}\bar{A}^{\kappa\lambda}_{pq}\bar{r}^{ij}_{\kappa\lambda}-\bar{A}^{rs}_{pq}\bar{r}^{ij}_{rs} \tag{16}$$

for A either r_{12} or $g_{12}=r_{12}^{-1}$, respectively, with the result

$$\mathscr{X}^{ij}_{rs}=\mathscr{X}^{rs}_{ij}=\tfrac{1}{2}\bar{R}^{\alpha\beta}_{rs}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}(\overline{r^2})^{ij}_{rs}-\tfrac{1}{2}\bar{r}^{pq}_{rs}\bar{r}^{ij}_{pq}, \tag{17a}$$

$$\mathscr{V}^{ij}_{rs}=\tfrac{1}{2}\bar{g}^{\alpha\beta}_{rs}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}\delta^{ij}_{rs}-\tfrac{1}{2}\bar{g}^{pq}_{rs}\bar{r}^{ij}_{pq}, \tag{17b}$$

$$\delta^{ij}_{rs}=\delta^{i}_{r}\delta^{j}_{s}-\delta^{i}_{s}\delta^{j}_{r}. \tag{17c}$$

Hence, any partial diagrams consisting of two vertices connected by a pair of lines with double arrows are easily evaluated. While the remaining $\mathscr{R}$ containing T diagrams [d3.15–d3.16 on Figs. 4(a) and 5(a)] are of the latter type, the $\mathscr{C}$ diagrams that remain from Fig. 6 can be divided to three categories.

(i) Diagrams that contain exclusively pairs of equivalent double arrowed lines as mentioned above [all from Fig. 6(a), except those under (ii)].
(ii) Diagrams coming from connected $\mathscr{R}$ clusters with inequivalent double arrowed lines (d6.2, d6.6, d6.11, d6.12). Their evaluation needs some nontrivial tricks[12] as outlined in the Appendices E and F.
(iii) Diagrams originating from disconnected $\frac{1}{2}\mathscr{R}^2$ clusters which do not contain equivalent double arrowed lines residing on a single vertex (d6.20, d6.21). These cannot be factorized within the actual basis and would lead to four-particle integrals. As it is shown in the Appendix G, these contributions can be neglected within the standard approximation A as well as B, they decrease with l as $(l+\frac{1}{2})^{-12}$.

Let us turn our attention to "critical" terms belonging to category (ii). The diagram d6.2 means explicitly

$$d6.2=\tfrac{1}{2}\mathscr{B}^{mn}_{kl}c^{ij}_{mn};\quad \mathscr{B}^{mn}_{kl}=\bar{R}^{\alpha\beta}_{kl}f^{\gamma}_{\beta}\bar{R}^{mn}_{\alpha\gamma}, \tag{18}$$

i.e., there is an f insertion between two $\mathscr{R}$ factors. The evaluation of products like $\bar{R}^{\alpha\beta}_{mn}f^{\gamma}_{\beta}\bar{R}^{ij}_{\alpha\gamma}$ is discussed in Appen-

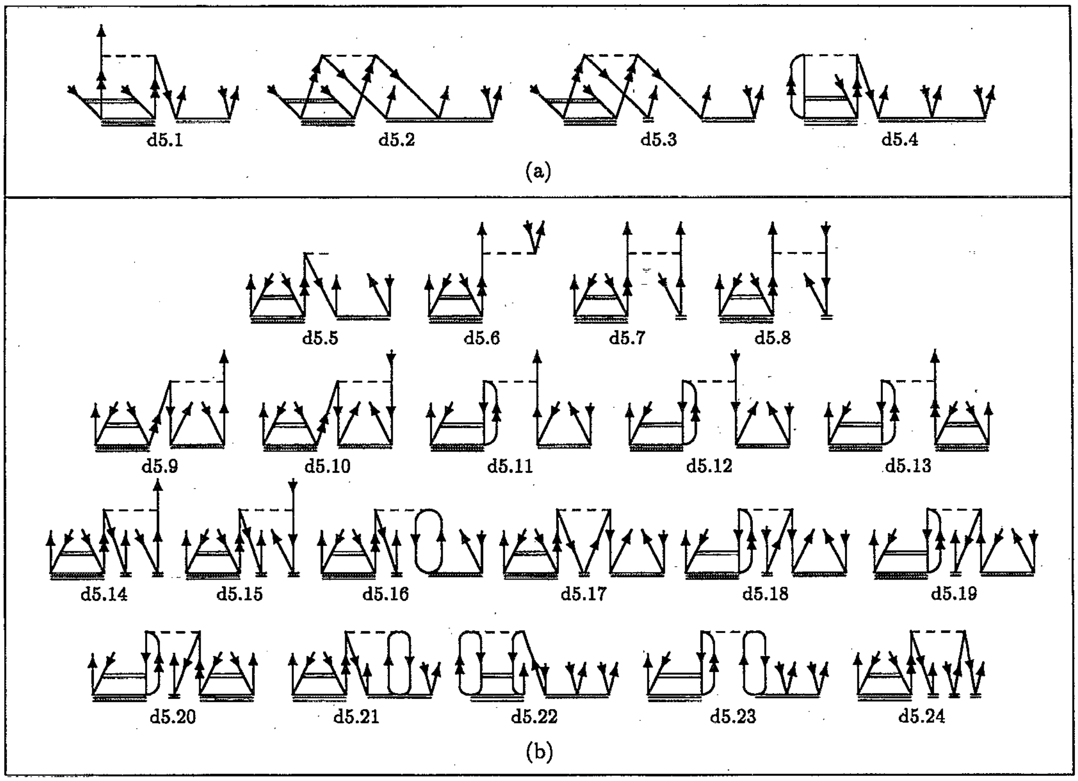

FIG. 5. $\mathscr{R}$ containing T_3 diagrams within the CC-R12 method. (a) Diagrams that remain in the standard approximation. (b) Diagrams that vanish due to the standard approximation.

dix E where a slightly improved approach to that of Ref. 12 is presented. If the extended Brillouin theorem is assumed to hold one can arrive at[23]

$$\mathscr{B}^{kl}_{ij} \overset{\text{s.a.}}{=} (-\mathscr{V}-\mathscr{V}^{\dagger}+\mathscr{U}+\mathscr{U}^{\dagger})^{kl}_{ij}+\tfrac{1}{2}(\mathscr{Q}+\mathscr{Q}^{\dagger}+\mathscr{F}+\mathscr{F}^{\dagger})^{kl}_{ij}, \tag{19a}$$

$$\mathscr{U}^{kl}_{ij}=\tfrac{3}{2}\,\delta^{kl}_{ij}-\tfrac{1}{2}\,\bar{r}^{pq}_{ij}\bar{u}^{kl}_{pq}, \tag{19b}$$

$$\mathscr{Q}^{kl}_{ij}=\mathscr{X}^{rl}_{ij}g^{mk}_{rm}+\mathscr{X}^{kr}_{ij}g^{ml}_{rm}=(\mathscr{Q}^{\dagger})^{ij}_{kl}, \tag{19c}$$

$$\mathscr{F}^{kl}_{ij}=\mathscr{X}^{ml}_{ij}f^{k}_{m}+\mathscr{X}^{km}_{ij}f^{j}_{m}=(\mathscr{F}^{\dagger})^{ij}_{kl}, \tag{19d}$$

$$\hat{u}=-\frac{1}{2r_{12}}\,\mathbf{r}_{12}(\boldsymbol{\nabla}_1-\boldsymbol{\nabla}_2). \tag{19e}$$

The explicit expressions of the diagrams d6.6, d6.11, and d6.12 listed under (ii) contain products of the type

$$\mathscr{Z}^{ij;l}_{mn;s}=\bar{R}^{\alpha\beta}_{mn}\bar{g}^{\nu l}_{\beta s}R^{ij}_{\alpha\gamma}, \tag{20a}$$

where we have used a semicolon in the sub- and superscripts to distinguish s,l as indices which are not equivalent with i,j or m,n. There is a one-sided g insertion between two $\mathscr{R}$ factors.

We must now specify the variants A and B of the standard approximation. While so far we have only neglected terms that vanish exactly in the atomic case provided that the basis is saturated up to a certain l value (and which probably decay exponentially with l in molecules), we are now obliged—as discussed previously[12]—to neglect terms that decay like l^{-m} with m sufficiently large. To be better than in conventional CC without r_{12} terms, where the energy increments go as l^{-4}, m must be larger than 4. The standard approximation A is characterized by $m=6$, and the standard approximation B by $m=8$. We have so far used the standard approximation A only in the context of second order perturbation theory, where it makes sense, since the computational effort for approximation B is comparable to that of third order perturbation theory. It is hence more economic to use a larger basis to reach the basis set limit than to apply approximation B. In all approaches going beyond MP2 we have always used approximation B.

It has been shown[12,28] that the terms involving exchange integrals $g^{s\gamma}_{\alpha l}$ in Eq. (20a) go as $(L+\frac{1}{2})^{-8}$ and can be neglected within the standard approximation both in variants A and B. The remaining terms go as $(L+\frac{1}{2})^{-6}$. Neglecting them implies an error $O(L^{-5})$. The "recommended" approximate expression for Eq. (20a) in the standard approximation B is as follows (see Appendix F)

$$\mathscr{Z}^{ij;s}_{kl;n}=\mathscr{Y}^{ij}_{rl}g^{rs}_{kn}+\mathscr{Y}^{ij}_{kr}g^{rs}_{ln}+\mathscr{Y}^{rj}_{kl}g^{in}_{rs}+\mathscr{Y}^{ir}_{kl}g^{jn}_{rs}+\mathbf{r}^{rq}_{kl}g^{ps}_{rn}\bar{r}^{ij}_{pq}, \tag{20b}$$

$$\mathscr{Y}^{ij}_{rs}=\mathscr{Y}^{rs}_{ij}=\mathscr{X}^{ij}_{rs}-\tfrac{1}{2}(\bar{r}^{2})^{ij}_{rs}. \tag{20c}$$

Irrespectively of which approximation for $\mathscr{B}$ and $\mathscr{Z}$ is chosen, it is important that all $\mathscr{R}$-containing diagrams that survive within the standard approximation are finally factorizable in terms of the given basis and the evaluation of no

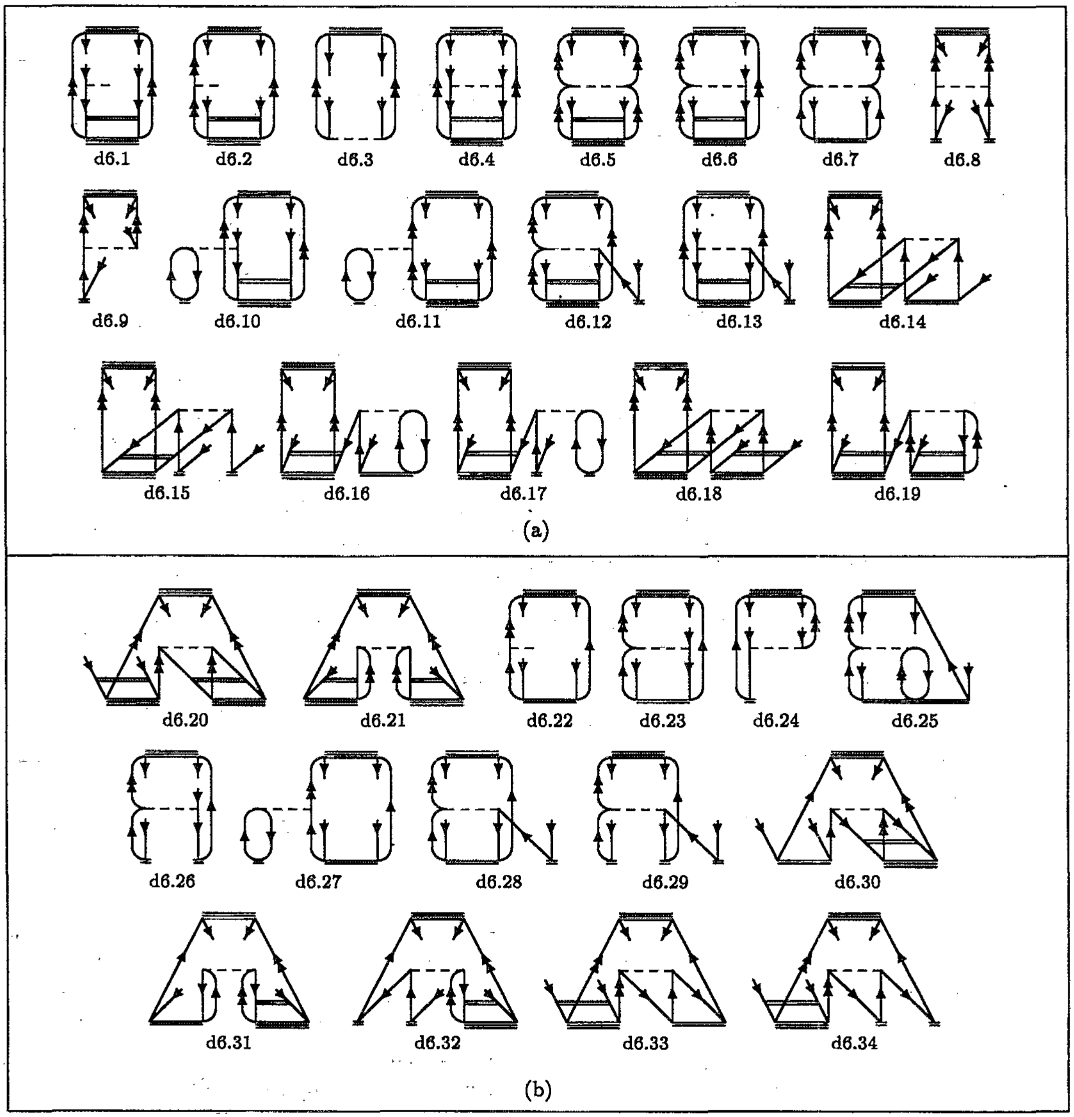

FIG. 6. $\mathscr{T}$ amplitude diagrams. (a) Diagrams that remain in the standard approximation. (b) Diagrams that vanish due to the standard approximation.

difficult three- or four-body integral is needed. Noting this, we can follow the established procedure of using intermediate effective interactions.[18,23,24,25,29] Unlike in the conventional CC, one can now also define amplitudeless intermediate interactions which need not be recalculated in each iteration. These result from the contraction of $\mathscr{R}_0$ with F_N or W_N as shown in Fig. 7. Their evaluation has been already mentioned above, except for

$$\mathscr{P}^{ij}_{mn}=\frac{1}{4}\bar{R}^{\alpha\beta}_{mn}\bar{g}^{\gamma\delta}_{\alpha\beta}\bar{R}^{ij}_{\gamma\delta} \tag{21}$$

which can be easily expressed using again just Eq. (16). For convenience, we have collected algebraic equivalents all of these amplitudeless intermediates in Table I, together with their spinfree counterparts as we will use them in Sec. VII. In Fig. 8 we complete the list of intermediate effective interactions as we have defined them for the use in the final CC-R12 equations (Fig. 9). Some of these intermediates are of course the same within the conventional approach. We present them just for completeness.

Explicit formulas in terms of a spinorbital basis are in Tables II and III. According to our previous classification of the CC variants,[18,30] these equations correspond to the full CCSDT-R12 method, CCSDT(4)-R12 is defined as a method in which nonlinear terms (via intermediates) with T_3 are neglected from Eq. (III.3), in CCSDT(3)-R12 all terms with T_3 contracted with W_N are neglected from Eq. (III.3) and from pertinent intermediates. CCSDT(2)-R12 corresponds to the further neglect of T_1 containing terms in the latter equation and, finally, in CCSDT(1)-R12 only linear T_2 contributions are preserved, since there is no valid non-zero contribution from the linear $\mathscr{R}$ contracted with W_N. Thus for CCSDT(1)-R12 the T_3 amplitude equations do not differ from the conventional ones.

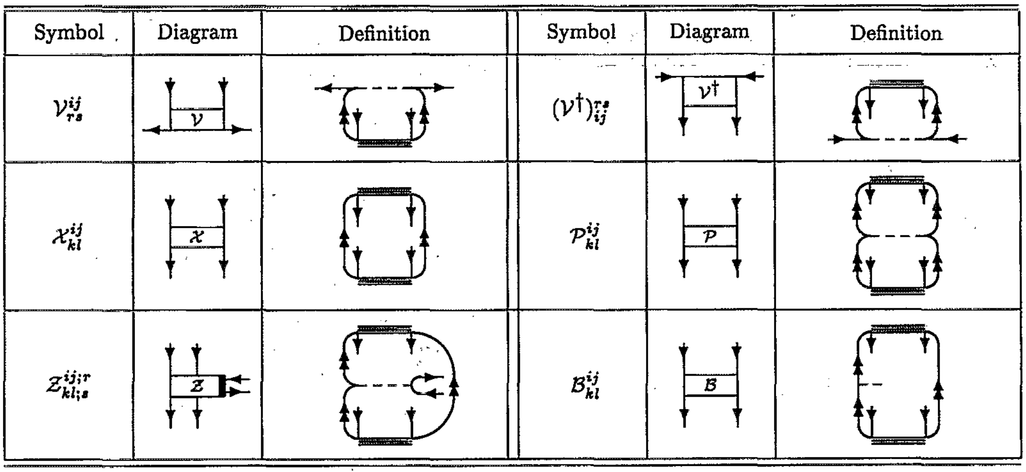

FIG. 7. The diagrammatic definition of S-amplitude independent effective intermediate interactions. Horizontal lines can be either particle or hole ones.

As it is seen from Eq. (III.4), the amplitudes of $\mathscr{C}$ in each iteration can not be expressed in such a simple way as the T amplitudes. Unlike for the T amplitudes it has turned out to be efficient to solve the set of Eqs. (III.4) in each iteration separately until convergency (i.e., with fixed intermediates). A convenient way appears to be a (sub)iterative solution in which the amplitudes in the $(k+1)$st subiteration are given as[16]

$$\mathbf{c}^{k+1} = -\mathscr{B}^{-1}\tilde{\tilde{\mathbf{c}}}^{k} \tag{22}$$

$\tilde{\tilde{\mathbf{c}}}$ includes all terms from the r.h.s. of Eq. (III.4).

From a formal point of view (see Appendix E) a part of the r.h.s. of Eq. (III.4) should be the shifted to the left side, namely, that which comes from the contraction of $\mathscr{B}$ with $\mathscr{F}_N$. This means we have to replace $\mathscr{B}^{kl}_{mn}$ by

$$\tilde{\mathscr{B}}^{kl}_{mn}(ij) = \mathscr{B}^{kl}_{mn} - \mathscr{X}^{kl}_{mn}(f^{i}_{i} + f^{j}_{j}). \tag{23}$$

The amplitudes of $\mathscr{C}$ are now calculated in each iteration as

$$\mathbf{c}_{ij}^{(k+1)} = -\tilde{\mathscr{B}}^{-1}(ij)\tilde{\mathbf{c}}_{ij}^{(k)}, \tag{24}$$

where $\tilde{\mathbf{c}}$ differs from $\tilde{\tilde{\mathbf{c}}}$ just by the last term in Eq. (23). The $\mathbf{c}_{ij}(\tilde{\mathbf{c}}_{ij})$ are columns of the matrix $\mathbf{c}(\tilde{\mathbf{c}})$ for the pair ij. In the starting macroiteration we set $\mathbf{c}=\mathbf{0}$, and the initial $\tilde{\mathbf{c}}$ is just represented by $\mathscr{V}^{\dagger}$.

Although Eq. (24) leads in most cases to faster convergence than Eq. (22) it is not yet sure whether Eq. (24) is always recommended. While in the limit of a complete basis $\tilde{B}(ij)$ is a positive definite matrix, this is not necessarily so for a rather small basis especially if large orbital energy differences $f^{m}_{m} - f^{n}_{n}$ are present. Further studies are necessary.

IV. COMPUTATIONAL ASPECTS

Let us first examine the intermediate effective interactions which must be recalculated in every iteration. In Table II one can find three $\mathscr{R}$-containing contributions the computation of which go roughly as $\sim n_0^6$ (II.1), as $\sim n_0^4(n_0+n_v)^2$ (II.2 second term) and as $\sim n_0^5$ (II.3 third term) where n_0 and n_v are the number of occupied (n_0) and virtual (n_v) spinorbitals, respectively. The T-amplitude Eqs. (III.1 to III.3) contain only one term (i.e., the last one in Eq. (II.1) which scales as $n_0^4 n_v$. If one realizes that the most time-consumming steps in the conventional CCSD equations go as $\sim n_v^4 n_0^2$ and $\sim n_v^3 n_0^3$, there is indeed just a tiny change in the computational demands for the T amplitudes as compared to conventional calculations at the CCSD level.

Consider now the $\mathscr{C}$-amplitude equation (III.4) in which the most time consumming steps involve a seven-index procedure (first two terms with $\mathscr{Z}$). In the worst case this means $\sim n_0^6 n_v$ (note that further factorization in the $\mathscr{Z}$ and T_1 containing terms is assumed). For the R12 calculations nearly saturated basis sets for the low l values have to be used. Hence, typically $n_v \gg n_0$ or $n_v > n_0^2$. This means that despite the seven-index procedure, the calculation of the $\mathscr{C}$ amplitudes requires a very minor part of a single CCSD iteration. At the CCSDT(n) levels the differences in computational demands for R12 and conventional approach practically disappear, since the calculation of T_3 amplitudes highly dominates in demands.

Let us briefly return to the intermediate effective interactions that do not depend on the amplitudes. As soon as appropriate r_{12}, r^2, and u integrals are available, the calculation of $\mathscr{V}$ and $\mathscr{X}$ is rather trivial. The calculation of $\mathscr{Z}$ needs a n^7 procedure, more precisely $\sim n_0^3(n_0+n_v)^4$ which is comparable with the calculation of triples in one iteration of CCSDT(1)-R12. The calculation of all needed integrals is nowadays not a real problem, since very effective algorithms have been implemented by Klopper and Röhse.[31] Since the computation of the AO integrals makes only a small fraction of the total computer time spent in general for correlation calculations (like CC or CI), the additional requirement to calculate r_{12} (or u_{12}) does practically not count.

If one would apply approximation A in CCSD-R12, the $\mathscr{Z}$-containing terms in Eq. (III.4) could be neglected. The last two terms in Eq. (III.4) have a $(L+\frac{1}{2})^{-6}$ dependence; but at the same time they contribute first at fifth order in the energy (in the sense of MBPT). Hence, they could be most probably neglected safely also in approximation B. This would save the $n_0^3 n_v^4$ procedure needed to calculate the per-

TABLE I. Explicit form of intermediate effective interactions from Fig. 7 in spinorbital basis (a) and within the orthogonally spin adapted theory (b).[a]

$$\mathscr{V}^{ij}_{rs}=\frac{1}{2}\bar{g}^{\alpha\beta}_{rs}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}\delta^{ij}_{rs}-\frac{1}{2}\bar{g}^{pq}_{rs}r^{ij}_{pq} \tag{I.1a}$$

$$\mathscr{V}^{IJ}_{RS}(\mu)\overset{\text{s.a.}}{=}\delta^{IJ}_{RS}(\mu)-\frac{1}{2}g^{PQ}_{RS}(\mu)r^{IJ}_{PQ}(\mu)\qquad\mu=0,1 \tag{I.1b}$$

$$(\mathscr{V}^{\dagger})^{rs}_{ij}=\frac{1}{2}\bar{R}^{\alpha\beta}_{ij}\bar{g}^{rs}_{\alpha\beta}\overset{\text{s.a.}}{=}\delta^{rs}_{ij}-\frac{1}{2}\bar{r}^{pq}_{ij}\bar{g}^{rs}_{pq} \tag{I.2a}$$

$$(\mathscr{V}^{\dagger})^{RS}_{IJ}(\mu)\overset{\text{s.a.}}{=}\delta^{RS}_{IJ}(\mu)-\frac{1}{2}r^{PQ}_{IJ}(\mu)g^{RS}_{PQ}(\mu)\qquad\mu=0,1 \tag{I.2b}$$

$$\mathscr{X}^{ij}_{kl}=\frac{1}{2}\bar{R}^{\alpha\beta}_{kl}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}(\overline{r^{2}})^{ij}_{kl}-\frac{1}{2}\bar{r}^{pq}_{kl}\bar{r}^{ij}_{pq} \tag{I.3a}$$

$$\mathscr{X}^{IJ}_{KL}(\mu)\overset{\text{s.a.}}{=}(r^{2})^{IJ}_{KL}(\mu)-\frac{1}{2}r^{PQ}_{KL}(\mu)r^{IJ}_{PQ}(\mu)\qquad\mu=0,1 \tag{I.3b}$$

$$\mathscr{P}^{ij}_{kl}=\frac{1}{4}\bar{R}^{\alpha\beta}_{kl}\bar{g}^{\gamma\delta}_{\alpha\beta}\bar{R}^{ij}_{\gamma\delta}\overset{\text{s.a.}}{=}-\frac{1}{2}\bar{r}^{pq}_{kl}\mathscr{V}^{ij}_{pq}=\frac{1}{4}\bar{r}^{pq}_{kl}\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs}-\bar{r}^{ij}_{kl} \tag{I.4a}$$

$$\begin{aligned}\mathscr{P}^{IJ}_{KL}(\mu)&\overset{\text{s.a.}}{=}-\frac{1}{2}r^{PQ}_{KL}(\mu)\mathscr{V}^{IJ}_{PQ}=\frac{1}{4}r^{PQ}_{KL}(\mu)g^{RS}_{PQ}(\mu)r^{IJ}_{RS}(\mu)\\&\quad-r^{IJ}_{KL}(\mu)\qquad\mu=0,1\end{aligned} \tag{I.4b}$$

$$\begin{aligned}\mathscr{Z}^{kl;t}_{ij;s}&=\bar{R}^{\alpha\beta}_{ij}\bar{g}^{\gamma t}_{\alpha s}\bar{R}^{kl}_{\gamma\beta}\overset{\text{s.a.}}{=}\mathscr{Y}^{rl}_{ij}g^{kt}_{rs}+\mathscr{Y}^{kr}_{ij}g^{lt}_{rs}+\mathscr{Y}^{rj}_{kl}g^{it}_{rs}+\mathscr{Y}^{ir}_{kl}g^{jt}_{rs}+\bar{r}^{rg}_{kl}g^{ps}_{rt}\bar{r}^{ij}_{pq}\\\mathscr{Y}^{rs}_{ij}&=\mathscr{Y}^{ij}_{rs}=\mathscr{X}^{ij}_{rs}-\frac{1}{2}(\overline{r^{2}})^{ij}_{rs}\end{aligned} \tag{I.5a}$$

$$\begin{aligned}\mathscr{Z}^{KL;T}_{IJ;S}(\mu)&\overset{\text{s.a.}}{=}\mathscr{Y}^{RL}_{IJ}(\mu)g^{KT}_{RS}+\mathscr{Y}^{KR}_{IJ}(\mu)g^{LT}_{RS}+\mathscr{Y}^{RJ}_{KL}(\mu)g^{LT}_{RS}\\&\quad+\mathscr{Y}^{IR}_{KL}(\mu)g^{JT}_{RS}+r^{RQ}_{KL}(\mu)g^{PS}_{RT}r^{IJ}_{PQ}(\mu)\\\mathscr{Y}^{RS}_{IJ}(\mu)&=\mathscr{Y}^{IJ}_{RS}(\mu)=\mathscr{X}^{IJ}_{RS}(\mu)-\frac{1}{2}(r^{2})^{IJ}_{RS}(\mu)\qquad\mu=0,1\end{aligned} \tag{I.5b}$$

$$\begin{aligned}\mathscr{B}^{ij}_{mn}&=\bar{R}^{\alpha\beta}_{mn}f^{\gamma}_{\alpha}\bar{R}^{ij}_{\gamma\beta}\overset{\text{s.a.}}{=}-\mathscr{V}^{ij}_{mn}-(\mathscr{V}^{\dagger})^{ij}_{mn}+\mathscr{U}^{ij}_{mn}+(\mathscr{U}^{\dagger})^{ij}_{mn}\\&\quad+\frac{1}{2}(\mathscr{Q}^{ij}_{mn}+(\mathscr{Q}^{\dagger})^{ij}_{mn}+\mathscr{F}^{ij}_{mn}+(\mathscr{F}^{\dagger})^{ij}_{mn})\\\mathscr{U}^{ij}_{mn}&=\frac{3}{2}\delta^{ij}_{mn}-\frac{1}{2}\bar{r}^{pq}_{mn}\bar{u}^{ij}_{pq};\quad\mathscr{Q}^{ij}_{mn}=\mathscr{X}^{rj}_{mn}g^{ki}_{rk}+\mathscr{X}^{ir}_{mn}g^{kj}_{rk}\\\mathscr{F}^{ij}_{mn}&=\mathscr{X}^{kj}_{mn}f^{i}_{k}+\mathscr{X}^{ik}_{mn}f^{j}_{k}\end{aligned} \tag{I.6a}$$

$$\begin{aligned}\mathscr{B}^{IJ}_{MN}(\mu)&\overset{\text{s.a.}}{=}-\mathscr{V}^{IJ}_{MN}(\mu)-(\mathscr{V}^{\dagger})^{IJ}_{MN}(\mu)+\mathscr{U}^{IJ}_{MN}(\mu)\\&\quad+(\mathscr{U}^{\dagger})^{IJ}_{MN}(\mu)+(\tfrac{1}{2})\,(\mathscr{Q}^{IJ}_{MN}(\mu)\\&\quad+(\mathscr{Q}^{\dagger})^{IJ}_{MN}(\mu)+\mathscr{F}^{IJ}_{MN}(\mu)+(\mathscr{F}^{\dagger})^{IJ}_{MN}(\mu))\\\mathscr{U}^{IJ}_{MN}(\mu)&=(\tfrac{3}{2})\,\delta^{IJ}_{MN}-(\tfrac{1}{2})\,r^{PQ}_{MN}(\mu)u^{IJ}_{PQ}(\mu);\quad\mathscr{Q}^{IJ}_{MN}(\mu)=\mathscr{X}^{RJ}_{MN}(\mu)g^{KI}_{RK}\\&\quad+\mathscr{X}^{IR}_{MN}(\mu)g^{KJ}_{RK}\\\mathscr{F}^{IJ}_{MN}(\mu)&=\mathscr{X}^{KJ}_{MN}(\mu)f^{I}_{K}+\mathscr{X}^{IK}_{MN}(\mu)f^{J}_{K}\qquad\mu=0,1\end{aligned} \tag{I.6b}$$

[a] Einstein summation convention is assumed, i.e., the expression is summed through all indices that do not match the target on the left-hand side.

$$\hat{u}=-\frac{1}{2r_{12}}\mathbf{r}_{12}(\boldsymbol{\nabla}_1-\boldsymbol{\nabla}_2);\quad\delta^{st}_{pr}=\delta^{s}_{p}\delta^{t}_{r}-\delta^{s}_{r}\delta^{t}_{p};\quad\delta^{ST}_{PR}(\mu)=\delta^{S}_{P}\delta^{T}_{R}+(-1)^{\mu}\delta^{S}_{R}\delta^{T}_{P}.$$

tinent $\mathscr{Z}$ intermediates at the beginning, as well as the $n_0^6 n_v$ step in every R12 subiteration. This approach has been used in our pilot calculations.[17] To use it routinely, still more numerical evidence is needed.

V. MBPT(2)-R12 AND MBPT(4)-R12: (MP2-R12 AND MP4-R12)

In the standard nondegenerate Rayleigh–Schrödinger PT with the Møller–Plesset partition of the Hamiltonian, i.e., with HF reference, W_N is formally the perturbation. Then for the first- and second-order corrections to the wave function one obtains (note that $E_1=0$ in this case)

$$-F_N|\Psi^{(1)}\rangle=QW_N|0\rangle, \tag{25a}$$

$$-F_N|\Psi^{(2)}\rangle=QW_N|\Psi^{(1)}\rangle, \tag{25b}$$

where Q is the projector into the complementary subspace orthogonal to the reference. Within the conventional approach $|\Psi^{(1)}\rangle$ and $|\Psi^{(2)}\rangle$ are expanded in a basis of Slater determinants. In the spirit of our R12 ansatz $\Psi^{(n)}$ is expanded in the basis of all possible functions generated by e^S. The pertinent nth order expansion coefficients $t^{(n)}$ and $c^{(n)}$ can be obtained from respective projections of Eqs. (25) onto the latter subspace. It follows then, that $t^{(1)}$ is not affected by $\mathscr{R}$ and the first order $c^{(1)}$ are determined by the diagrams d6.1–d6.3. For the canonical HF reference we get

$$(t^{ij^{(1)}}_{ab})_{R12}=(t^{ij^{(1)}}_{ab})_{\text{conv}}=(D^{ijab}_{ijab})^{-1}\bar{g}^{ij}_{ab}, \tag{26a}$$

$$-\tfrac{1}{2}\tilde{\mathscr{B}}^{mn}_{kl}(ij)c^{ij^{(1)}}_{mn}=(\mathscr{V}^{\dagger})^{ij}_{kl}=\mathscr{V}^{kl}_{ij}. \tag{26b}$$

At this point, i.e., limiting oneself to first order in $S=T+\mathscr{R}$ and second order in E, we may alternatively consider approximation A, in which $\mathscr{B}$ given fully by Eq. (E.20) is reduced to

$$-\tfrac{1}{2}\tilde{\mathscr{B}}^{mn}_{kl}(ij)=\tfrac{1}{2}(-\mathscr{V}-\mathscr{V}^{\dagger}+\mathscr{U}+\mathscr{U}^{\dagger})^{mn}_{kl}. \tag{26c}$$

It might be more consistent to include as well the terms in $\mathscr{X}f$, but this has so far not be done as the default option within the standard approximation A. Noting that in the limit of a complete basis

$$\begin{aligned}&\mathscr{B}^{-1}\mathscr{V}\rightarrow\frac{1}{2}\quad\text{for natural singlet states.}\\&\mathscr{B}^{-1}\mathscr{V}\rightarrow\frac{1}{4}\quad\text{for triplet states.}\end{aligned} \tag{26d}$$

a good diagnostic of near completeness of the basis is the ratio

$$\mathrm{Tr}(\mathscr{V})/\mathrm{Tr}(\mathscr{B}) \tag{26e}$$

taken separately for singlet and triplet pairs.

R12 corrections to the second order T amplitudes originate in the diagrams d4.2 and d4.4 at the levels of singles and doubles, respectively. There is no R12 second order wave function contribution at the level of triples within the standard approximation. The projection of the l.h.s. of Eq. (26b) onto the subspace of the R12 functions is given by the diagrams d6.4–d6.7 (provided that amplitudes in these diagrams are of first order) while the r.h.s. of the pertinent equation is again given by d6.1 and d6.2 (with second order amplitudes). Hence,

$$(t^{ij^{(2)}}_{ab})_{R12}=(t^{ij^{(2)}}_{ab})_{\text{conv}}+\tfrac{1}{2}\mathscr{V}^{kl}_{ab}c^{ij^{(1)}}_{kl}(D^{ijab}_{ijab})^{-1}, \tag{27a}$$

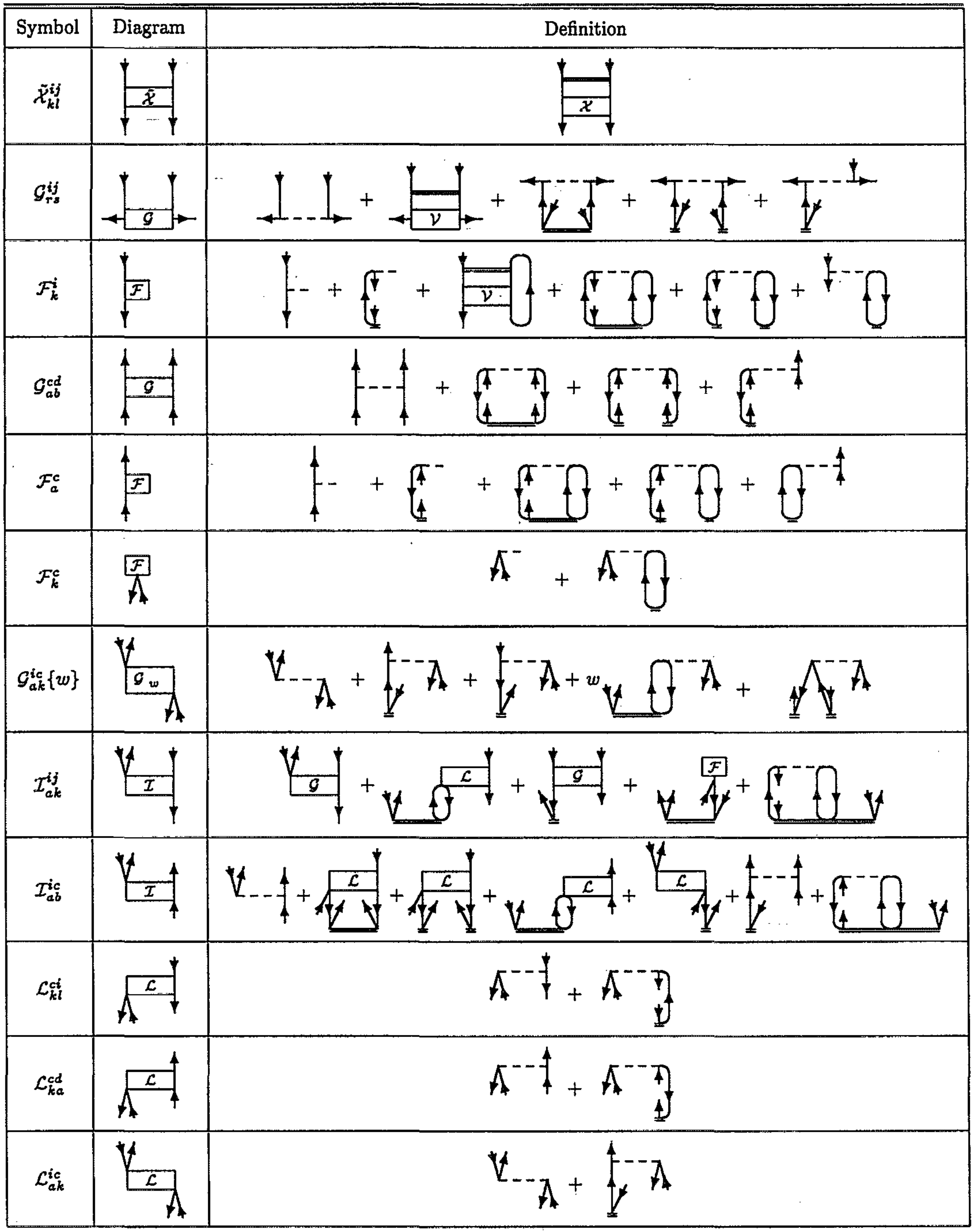

FIG. 8. The diagrammatic definition of S-amplitude dependent effective intermediate interactions. Horizontal lines mean that modifications with either hole or particle lines are possible. Superscripts (subscripts) denote incoming (outgoing) open lines from the left to the right.

$$(t_a^{i^{(2)}})_{R12}=(t_a^{i^{(2)}})_{\text{conv}}+\tfrac{1}{2}\mathscr{V}^{\,kl}_{\,am}c^{im^{(1)}}_{kl}(D^{ia}_{ia})^{-1}, \tag{27b}$$

$$(t^{ijk^{(2)}}_{abc})_{R12}=(t^{ijk^{(2)}}_{abc})_{\text{conv}}, \tag{27c}$$

$$\begin{aligned}-\tfrac{1}{2}\tilde{\mathscr{B}}^{\,mn}_{\,kl}(ij)c^{ij^{(2)}}_{mn}={}&\tfrac{1}{4}\mathscr{X}^{\,m_1n_1}_{\,kl}c^{mn^{(1)}}_{m_1n_1}\bar{g}^{ij}_{mn}+\tfrac{1}{2}\mathscr{P}^{\,mn}_{\,kl}c^{ij^{(1)}}_{mn}\\&+\tfrac{1}{2}(\mathscr{Z}^{mn;j}_{kl;n_1}c^{in_1^{(1)}}_{mn}+\mathscr{Z}^{mn;i}_{kl;n_1}c^{n_1j^{(1)}}_{mn})\\&+\tfrac{1}{2}(\mathscr{V}^{\dagger})^{cd}_{kl}t^{ij^{(1)}}_{cd},\end{aligned} \tag{27d}$$

whereas second order coefficients formally due to quadruples are given as products of first order ones. Starting the coupled cluster calculation with zero amplitudes in the first iteration, the f_1 in Eq. (14a) vanishes, while Eq. (14b) provides $t^{ij^{(1)}}_{ab}$, and Eq. (III.4) reduces to Eq. (26b). Similarly, the CC equations can be easily modified to obtain the amplitudes of Eq. (27) in the second iteration. Then, using Wigner's $2n+1$ rule and the linked diagram theorem we get the energetic contributions

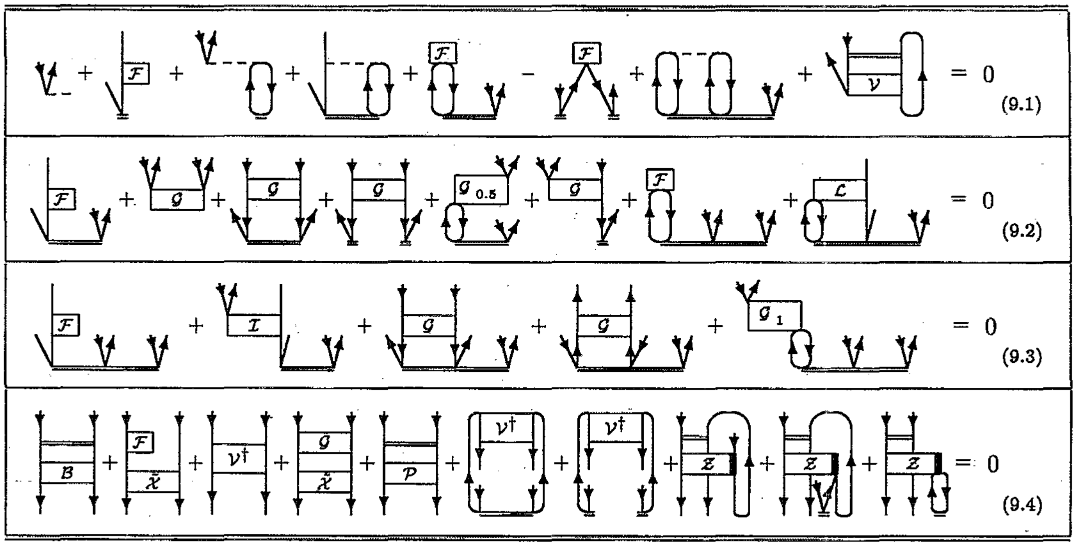

FIG. 9. The diagrammatic form of CCSDT-R12 equations using the intermediates from Fig. 8. For the arrowless open lines both possible modifications must be accounted for.

$$\Delta E_D^{(2)}=(\Delta E_D^{(2)})_{\text{conv}}, \tag{28a}$$

$$\Delta E_{\mathscr{R}}^{(2)}=\tfrac{1}{4}\mathscr{V}\,_{ij}^{kl}c_{kl}^{ij^{(1)}}, \tag{28b}$$

$$\Delta E_D^{(3)}=\tfrac{1}{4}\bar{g}_{ij}^{ab}(t_{ab}^{ij^{(2)}})_{R12}, \tag{28c}$$

$$\Delta E_{\mathscr{R}}^{(3)}=\tfrac{1}{4}\mathscr{V}\,_{ij}^{kl}c_{kl}^{ij^{(2)}}, \tag{28d}$$

$$\Delta E_S^{(4)}=(t_a^{i^{(2)}})_{R12}(t_a^{i^{(2)}})_{R12}D_{ia}^{ia}, \tag{28e}$$

$$\Delta E_D^{(4)}=\tfrac{1}{4}(t_{ab}^{ij^{(2)}})_{R12}(t_{ab}^{ij^{(2)}})_{R12}D_{ijab}^{ijab}, \tag{28f}$$

$$\Delta E_{\mathscr{R}}^{(4)}=-\tfrac{1}{8}c_{ij}^{mn(2)}c_{kl}^{mn(2)}\tilde{\mathscr{B}}\,_{kl}^{ij}(mn), \tag{28g}$$

TABLE II. Explicit forms of the intermediate effective interactions from Fig. 8 in spinorbital basis.[a]

$\tilde{\mathscr{X}}\,_{kl}^{ij}=\frac{1}{2}\,\mathscr{X}\,_{kl}^{mn}c_{mn}^{ij}$	(II.1)
$\mathscr{G}\,_{rs}^{ij}=\bar{g}_{rs}^{ij}+\frac{1}{2}\,\mathscr{V}\,_{rs}^{mn}c_{mn}^{ij}+\frac{1}{2}\,\bar{g}_{rs}^{cd}\tau\,_{cd}^{ij}+(\bar{g}_{rs}^{dj}t_d^i+\bar{g}_{rs}^{id}t_d^i)$	(II.2)
$\mathscr{F}\,_k^i=f\,_k^i+f_k^ct_c^i+\frac{1}{2}\,\mathscr{V}\,_{kj}^{mn}c_{mn}^{ij}+\frac{1}{2}\,\bar{g}_{kj}^{cd}\tau\,_{cd}^{ij}+\bar{g}_{kj}^{ic}t_c^j$	(II.3)
$\mathscr{G}\,_{ab}^{cd}=\bar{g}_{ab}^{cd}+\frac{1}{2}\,\bar{g}_{kl}^{cd}\tau\,_{ab}^{kl}-(\bar{g}_{lb}^{cd}t_a^l+\bar{g}_{al}^{cd}t_b^l)$	(II.4)
$\mathscr{F}\,_a^c=f_a^c-f_k^ct_a^k-\frac{1}{2}\,\bar{g}_{kl}^{cd}\tau\,_{ad}^{kl}+\bar{g}_{al}^{cd}t_d^l$	(II.5)
$\mathscr{F}_k^c=f_k^c+\bar{g}_{kl}^{cd}t_d^l$	(II.6)
$\mathscr{G}\,_{ak}^{ic}\{w\}=\bar{g}_{ak}^{ic}+\bar{g}_{ak}^{dc}t_d^i-\bar{g}_{lk}^{ic}t_a^l+\bar{g}_{kl}^{cd}(w.t_{da}^{li}-t_a^lt_d^i)$	(II.7)
$\mathscr{I}\,_{ak}^{ij}=\mathscr{G}\,_{ak}^{ij}+(\mathscr{L}\,_{lk}^{cj}t_{ca}^{li}+\mathscr{L}\,_{kl}^{ci}t_{ca}^{lj})-\mathscr{G}\,_{lk}^{ij}t_a^l+\mathscr{F}\,_k^ct_{ac}^{ij}+\frac{1}{2}\,\bar{g}_{kl}^{cd}t_{acd}^{ijl}$	(II.8)
$\mathscr{I}\,_{ab}^{ic}=\bar{g}_{ab}^{ic}+\frac{1}{2}\,\mathscr{L}\,_{kl}^{ci}\tau_{ba}^{kl}+(\mathscr{L}\,_{lb}^{dc}t_{da}^{li}+\mathscr{L}\,_{la}^{cd}t_{db}^{li})$ $-(\mathscr{L}\,_{al}^{ic}t_b^l-\mathscr{L}\,_{bl}^{ic}t_a^l)+\bar{g}_{ab}^{cd}t_d^l-\frac{1}{2}\,\bar{g}_{kl}^{cd}t_{abd}^{ikl}$	(II.9)
$\mathscr{L}\,_{kl}^{ci}=\bar{g}_{kl}^{ci}+\bar{g}_{kl}^{cd}t_d^i$	(II.10)
$\mathscr{L}\,_{ka}^{cc}=\bar{g}_{ka}^{cd}-\bar{g}_{kl}^{cd}t_a^l$	(II.11)
$\mathscr{L}\,_{ak}^{ic}=\bar{g}_{ak}^{ic}+\bar{g}_{ak}^{dc}t_d^i$	(II.12)

[a]See Table I. $\tau\,_{ab}^{ij}=t_{ab}^{ij}+t_a^it_b^j-t_a^jt_b^i$. In (II.7) w may have the values $\frac{1}{2}$ or 1.

$$\Delta E_T^{(4)}=(\Delta E_T^{(4)})_{\text{conv}}, \tag{28h}$$

$$\Delta E_Q^{(4)}=\Delta E_{DD}^{(4)}=(\Delta E_Q^{(4)})_{\text{conv}}, \tag{28i}$$

$$\Delta E_{D\mathscr{R}}^{(4)}=\tfrac{1}{4}\mathscr{O}_{ij}^{kl}\tilde{\mathscr{V}}\,_{kl}^{ij}-\mathscr{O}_{il}^{kl}\tilde{\mathscr{V}}\,_{km}^{im}+\tfrac{1}{4}\tilde{\mathscr{O}}\,_{ij}^{kl}\tilde{\mathscr{X}}\,_{kl}^{ij(1)}-\tilde{\mathscr{O}}\,_{il}^{kl}\tilde{\mathscr{X}}\,_{km}^{im(1)}, \tag{28j}$$

$$\Delta E_{\mathscr{R}\mathscr{R}}^{(4)}=\tfrac{1}{4}\tilde{\mathscr{V}}\,_{ij}^{kl}\tilde{\mathscr{X}}\,_{kl}^{ij(1)}-\tilde{\mathscr{V}}\,_{il}^{kl}\tilde{\mathscr{X}}\,_{km}^{im(1)}, \tag{28k}$$

where $\tilde{\mathscr{X}}\,^{(1)}$ means that it is calculated in terms of $c^{(1)}$. We have further used

$$\mathscr{O}\,_{ij}^{kl}=\tfrac{1}{2}t_{ab}^{ij^{(1)}}t_{ab}^{kl^{(1)}}, \tag{29a}$$

$$\tilde{\mathscr{O}}\,_{ij}^{kl}=\tfrac{1}{2}\bar{g}_{ab}^{kl}t_{ij}^{ab^{(1)}}, \tag{29b}$$

$$\tilde{\mathscr{V}}\,_{ij}^{kl}=\tfrac{1}{2}\mathscr{V}\,_{ij}^{mn}c_{mn}^{kl^{(1)}}. \tag{29c}$$

The subscripts on ΔE distinguish contributions due to the pertinent excitations or the R12 correction (for $\mathscr{R}$). $E_{DD}^{(4)}$ just stresses that $E_Q^{(4)}$ originates from the product of doubles. The last two contributions come also formally from quadruple excitations but originate from the product of $\mathscr{R}$ with T_2 (or $\mathscr{R}$). Closing the diagrams d4.6 and d4.8 with T_2 and d6.14, d6.16 with $\mathscr{C}$ (assuming the appropriate first order amplitudes) one obtains $E_{D\mathscr{R}}^{(4)}$, while $E_{\mathscr{R}\mathscr{R}}^{4}$ can be obtained by closing diagrams d6.18 and d6.19 with $\mathscr{C}$. We note that in Eqs. (27) we have not considered contributions that vanish within the standard approximation.

The only level at which the conventional energy completely decouples from the cusp correction is the MBPT(2)-R12, i.e., in the initial cycle of the CC iteration procedure. Then both the conventional correlation energy and the cusp correction can be independently calculated.

TABLE III. Spinorbital form of the CCSDT-R12 equations.[a]

$$D^{ia}_{ia}t^{i}_{a}=f^{i}_{a}+\tilde{\mathscr{F}}^{c}_{a}t^{i}_{c}-\tilde{\mathscr{F}}^{i}_{k}t^{k}_{a}+\bar{g}^{ic}_{ak}t^{k}_{c}+\frac{1}{2}\bar{g}^{dc}_{ak}t^{ik}_{dc}-\frac{1}{2}\bar{g}^{ci}_{kl}t^{kl}_{ca}$$
$$+\mathscr{F}^{c}_{k}(t^{ki}_{ca}+t^{k}_{a}t^{i}_{c})+\frac{1}{4}\bar{g}^{cd}_{kl}t^{kli}_{cda}+\frac{1}{2}\mathscr{V}^{kl}_{am}c^{im}_{kl} \qquad \text{(III.1)}$$

$$D^{ijab}_{ijab}t^{ij}_{ab}=(\tilde{\mathscr{F}}^{c}_{a}t^{ij}_{cb}+\tilde{\mathscr{F}}^{a}_{b}t^{ij}_{ac})-(\tilde{\mathscr{F}}^{i}_{k}t^{kj}_{ab}+\tilde{\mathscr{F}}^{j}_{k}t^{ik}_{ab})+\mathscr{G}^{ij}_{ab}$$
$$+\frac{1}{2}\mathscr{G}^{ij}_{kl}\tau^{kl}_{ab}+\sum_{P_{ij}P_{ab}}(-1)^{p}\mathscr{G}^{ic}_{ak}\{0.5\}t^{kj}_{cb}$$
$$-(\mathscr{G}^{ij}_{ak}t^{k}_{b}+\mathscr{G}^{ij}_{kb}t^{k}_{a})+\mathscr{F}^{c}_{k}t^{ijk}_{abc}-\frac{1}{2}(\mathscr{L}^{ci}_{kl}t^{klj}_{cab}$$
$$+\mathscr{L}^{cj}_{kl}t^{kil}_{cab})+\frac{1}{2}(\mathscr{L}^{cd}_{ka}t^{kij}_{cdb}+\mathscr{L}^{cd}_{kb}t^{kij}_{cad}) \qquad \text{(III.2)}$$

$$D^{ijkabc}_{ijkabc}t^{ijk}_{abc}=\sum_{P^{+}_{abc}}\tilde{\mathscr{F}}^{d}_{a}t^{ijk}_{dbc}-\sum_{P^{+}_{ijk}}\tilde{\mathscr{F}}^{i}_{l}t^{ljk}_{abc}$$
$$+\sum_{P^{+}_{ijk}}\sum_{P^{+}_{abc}}(\mathscr{G}^{id}_{ab}t^{jk}_{dc}-\mathscr{G}^{ij}_{al}t^{lk}_{bc})$$
$$+\frac{1}{2}\sum_{P^{+}_{ijk}}\mathscr{G}^{ij}_{lm}t^{lmk}_{abc}+\frac{1}{2}\sum_{P^{+}_{abc}}\mathscr{G}^{de}_{ab}t^{ijk}_{dec}$$
$$+\sum_{P^{+}_{ijk}}\sum_{P^{+}_{abc}}\mathscr{G}^{id}_{al}\{1\}t^{ljk}_{dbc} \qquad \text{(III.3)}$$

$$-\frac{1}{2}\mathscr{B}^{mn}_{kl}c^{ij}_{mn}=-(\mathscr{F}^{j}_{m}\tilde{\mathscr{X}}^{im}_{kl}+\mathscr{F}^{i}_{m}\tilde{\mathscr{X}}^{mj}_{kl})+(\mathscr{V}^{\dagger})^{ij}_{kl}+\frac{1}{2}\mathscr{G}^{ij}_{mn}\tilde{\mathscr{X}}^{mn}_{kl}$$
$$+\frac{1}{2}\mathscr{P}^{mn}_{kl}c^{ij}_{mn}+\frac{1}{2}(\mathscr{V}^{\dagger})^{ab}_{kl}\tau^{ij}_{ab}-\frac{1}{2}(\mathscr{Z}^{mn;j}_{kl;o}c^{io}_{mn}$$
$$+\mathscr{Z}^{mn;i}_{kl;o}c^{oj}_{mn})-\frac{1}{2}(\mathscr{Z}^{mn;a}_{kl;o}c^{io}_{mn}t^{j}_{a}+\mathscr{Z}^{mn;a}_{kl;o}c^{oj}_{mn}t^{i}_{a})$$
$$+\frac{1}{2}\mathscr{Z}^{mn;a}_{kl;o}c^{ij}_{mn}t^{o}_{a} \qquad \text{(III.4)}$$

[a] See Table I. $P_{rs..}$ means permutations of pertinent indices, while p (in III.2) denotes the total parity of the permutation. $P^{+}_{rs..}$ means permutations with positive parity. See Table II for definition of intermediates. $\tilde{\mathscr{F}}^{r}_{s}=\mathscr{F}^{r}_{s}-f^{r}_{s}\delta^{s}_{r}$; $D^{ij..ab..}_{ij..ab..}=f^{i}_{i}+f^{j}_{j}+\cdots-f^{a}_{a}-f^{b}_{b}-\cdots$.

VI. NONITERATIVE CORRECTIONS TO THE CC-R12 ENERGY

After the CC calculation at a specific level of theory it has turned out to be efficient to approximate the energetic contributions due to certain types of missing higher excitations by their MBPT-like counterparts, using the available CC amplitudes instead of those resulting from perturbation theory itself. These contributions either complete the energy to be correct to the certain order of MBPT or approximate the higher version of CC by adding the most important missing terms. To the former type belong, e.g., T(CCSD) [i.e., the difference between CCSD[T] and CCSD][18] and fifth order corrections[32,33]) to the latter one the frequently used CCSD(T).[34] As it is well known,

$$T(\text{CCSD})=-\langle 0|(T_3^{[2]\dagger}F_N T_3^{[2]})_C|0\rangle \qquad (30)$$

completes the energy to be correct to fourth order (in terms of MBPT).

$$-\langle 0|\tilde{a}^{ijk}_{abc}F_N T_3^{[2]}|0\rangle=\langle 0|\tilde{a}^{ijk}_{abc}(W_N T_2)_C|0\rangle. \qquad (31)$$

Nothing is changed within the R12 approach since the linear $(W_N\mathscr{R})$ contribution to T_3 vanishes due to the standard approximation. It means that T(CCSD) is only indirectly affected by $\mathscr{R}$ via T_2 at the fifth-order level. In addition to T(CCSD), CCSD(T) includes a fifth-order term

$$\Delta E^{[5]}_{\text{ST}}=\langle 0|(T_1^{\dagger}W_N T_3^{[2]})|0\rangle. \qquad (32)$$

While in CCSDT-1 (exactly only at the fifth-order level) this term as well as its hermitian conjugate appears, CCSD covers only one of those terms.[33,34] Hence, CCSD(T) represents an approximation to CCSDT-1. Since the lowest (i.e., second order) order contributions to T_1 originate from the contraction of W_N with T_2 as well as with $\mathscr{R}$ (see Table III) the change in $\Delta E^{[5]}_{ST}$ on going from conventional to R12 may be expected to be relatively larger. However, compared to the conventional CC method, there is still no formal change as to the calculation of CCSD(T) as soon as the amplitudes are available.

Because of its computational complexity, it is less common to correct for the rest of the fifth-order terms which have their origin in connected triple and quadruple excitations.[32,33] Let us very briefly mention how these corrections would be affected within the R12 theory.

Starting from converged CCSD, the final energy is given as[32]

$$\Delta E_{\text{conv}}=\Delta E_{\text{CCSD(T)}}+\Delta E^{[5]}_{TT}+\Delta E^{[5]}_{TD}+\Delta E^{[5]}_{QQ}+\Delta E^{[5]}_{QT}. \qquad (33a)$$

The R12 approach will include additional terms

$$\begin{aligned}\Delta E&=\Delta E_{\text{conv}}+\Delta E_{R12},\\ &=\Delta E_{\text{conv}}+(\langle 0|\mathscr{R}^{\dagger}T_2^{\dagger}W_N T_3^{[2]}|0\rangle+\text{h.c.})\\ &\quad+\langle 0|\mathscr{R}^{\dagger}T_2^{\dagger}(W_N T_2\mathscr{R})_C|0\rangle\\ &\quad+\tfrac{1}{4}\langle 0|\mathscr{R}^{\dagger}\mathscr{R}^{\dagger}(W_N\mathscr{R}\mathscr{R})_C|0\rangle,\end{aligned} \qquad (33b)$$

while other possible terms vanish within the standard approximation. Of course, in Eq. (33b) "conv" means formally the expression (33a) with the amplitudes from CCSD-R12. It is not the purpose of this paper to derive a more explicit form of Eq. (33b). Let us remember that for the calculation of the noniterative corrections the amplitudes of $T^{\dagger}$ are assumed to have the same values as the amplitudes of T.

VII. ORTHOGONALLY SPIN ADAPTED FORMULATION OF CCSDT-R12

The spin adaptation within the coupled cluster theory has been a topic of several recent and older papers.[35–39] We essentially followed the orthogonally spin adapted theory as it was presented by Paldus *et al.*[36] and by Kutzelnigg.[37] The theory is based on the projection of Eq. (7) onto an orthogonal set of spin-adapted excited configurations which, for the closed shell case (singlet states), result from $|0\rangle$ through an action of the following excitation operators (capital letters will label the spinfree orbitals):

$$E^{A}_{I}=\tilde{E}^{A}_{I}, \qquad (34a)$$

$$E^{AB}_{IJ}(0)=\tfrac{1}{2}(\tilde{E}^{AB}_{IJ}+\tilde{E}^{BA}_{IJ}), \qquad (34b)$$

$$E^{AB}_{IJ}(1)=\tfrac{1}{2}(\tilde{E}^{AB}_{IJ}-\tilde{E}^{BA}_{IJ}), \qquad (34c)$$

$$E_{IJK}^{ABC}(1)=\tfrac{1}{6}(2\tilde{E}_{IJK}^{ABC}+2\tilde{E}_{IJK}^{BAC}-\tilde{E}_{IJK}^{BCA}-\tilde{E}_{IJK}^{CAB}-\tilde{E}_{IJK}^{ACB} -\tilde{E}_{IJK}^{CBA})\quad \mathscr{S}\equiv\{0,0,\tfrac{1}{2}\}, \tag{34d}$$

$$E_{IJK}^{ABC}(2)=\frac{\sqrt{3}}{6}(-\tilde{E}_{IJK}^{BCA}+\tilde{E}_{IJK}^{CAB}-\tilde{E}_{IJK}^{ACB}+\tilde{E}_{IJK}^{CBA}) \quad \mathscr{S}\equiv\{1,0,\tfrac{1}{2}\}, \tag{34e}$$

$$E_{IJK}^{ABC}(3)=\frac{\sqrt{3}}{6}(+\tilde{E}_{IJK}^{BCA}-\tilde{E}_{IJK}^{CAB}-\tilde{E}_{IJK}^{ACB}+\tilde{E}_{IJK}^{CBA}) \quad \mathscr{S}\equiv\{0,1,\tfrac{1}{2}\}, \tag{34f}$$

$$E_{IJK}^{ABC}(4)=\tfrac{1}{6}(2\tilde{E}_{IJK}^{ABC}-2\tilde{E}_{IJK}^{BAC}-\tilde{E}_{IJK}^{BCA}-\tilde{E}_{IJK}^{CAB}+\tilde{E}_{IJK}^{ACB} +\tilde{E}_{IJK}^{CBA})\quad \mathscr{S}\equiv\{1,1,\tfrac{1}{2}\} \tag{34g}$$

$$E_{IJK}^{ABC}(5)=\tfrac{1}{6}(\tilde{E}_{IJK}^{ABC}-\tilde{E}_{IJK}^{BAC}+\tilde{E}_{IJK}^{BCA}+\tilde{E}_{IJK}^{CAB}-\tilde{E}_{IJK}^{ACB} -\tilde{E}_{IJK}^{CBA})\quad \mathscr{S}\equiv\{1,1,\tfrac{3}{2}\} \tag{34h}$$

where the spin-free counterparts of the excitation operators are [in Eq. (35) α,β are exceptionally related to spin][37]

$$\tilde{E}_P^Q=a_{P\alpha}^{Q\alpha}+a_{P\beta}^{Q\beta};\quad \tilde{E}_{PQ..}^{TU..}=\tilde{E}_P^T\tilde{E}_Q^U. \tag{35}$$

The parameters in parentheses are connected with intermediate internal spin quantum numbers. 0 and 1 for biexcitations correspond to intermediate singlet and intermediate triplet coupling, respectively. $\mathscr{S}\equiv\{S^{12},S_{12},S_i\}$ distinguishes the five linearly independent triple excitations with $S^{12}(S_{12})$ being the intermediate spin quantum number for the first two holes (particles) while S_i denotes the total intermediate spin quantum numbers. All configuration states defined by the operators (34) are essentially the same as those from Ref. 36, except for the normalization. Since the final equations are simpler, we have omitted both the normalization due to the multiplicity and due to the repeated indices.

Operators like those defined by Eqs. (34b) and (34c), but normalized differently have also been symbolized as $\overset{+}{E}{}_{IJ}^{AB}$ and $\overset{-}{E}{}_{IJ}^{AB}$, respectively.[37] An analogous notation has been used for the integrals of type (36).

Amplitudes corresponding to spinfree configurations will be denoted similarly as operators in Eq. (34) [i.e., with suffix "(i)"]. It is useful to define symmetrized (antisymmetrized) integrals of two electron operators, corresponding to intermediate (unnormalized) singlet (triplet) states

$$Y_{PQ}^{RS}(0)=Y_{PQ}^{RS}+Y_{PQ}^{SR}, \tag{36a}$$

$$Y_{PQ}^{RS}(1)=Y_{PQ}^{RS}-Y_{PQ}^{SR}. \tag{36b}$$

Then the H_N can be redefined[37] (Greek letters in the following two equations refer to spin-free orbitals within the complete basis):

$$F_N=f_\kappa^\lambda\tilde{E}_\lambda^\kappa;\quad W_N=\tfrac{1}{4}(g_{\kappa\lambda}^{\mu\nu}(0)E_{\nu\mu}^{\kappa\lambda}(0)+g_{\kappa\lambda}^{\mu\nu}(1)E_{\nu\mu}^{\kappa\lambda}(1)). \tag{37}$$

Similarly the spinfree operator $\mathscr{R}$ is given as a sum

$$\mathscr{R}=\tfrac{1}{8}(c_{KL}^{IJ}(0)R_{\alpha\beta}^{KL}(0)E_{IJ}^{\alpha\beta}(0)+c_{KL}^{IJ}(1)R_{\alpha\beta}^{KL}(1)E_{IJ}^{\alpha\beta}(1)). \tag{38}$$

Although the so-called nonorthogonally spin adapted theory[35] seems to be more transparent, the orthogonally spin-adapted theory leads directly to an efficient algorithm. The reason is that amplitudes and intermediates possess the same symmetry properties as the orthogonally spin adapted states do. Actually, to achieve the optimal algorithm within the nonorthogonal spin-adapted theory such (anti)symmetrizations are used.[40] Orthogonally spin-adapted theory works with a minimal number of amplitudes which in the case of triples means reduction from six amplitudes handled in the nonorthogonal theory to five linearly independent amplitudes belonging to a given set of indices (IJK,ABC).[36]

Concerning the theory outside the R12 context, the reader is referred to the above mentioned original papers. However, before giving explicit equations it is useful to remind the symmetry properties of the amplitudes. For the T_2 and $\mathscr{C}$ amplitudes we have

$$t_{AB}^{IJ}(0)=t_{BA}^{IJ}(0)=t_{AB}^{JI}(0)=t_{BA}^{JI}(0), \tag{39a}$$

$$t_{AB}^{IJ}(1)=-t_{BA}^{IJ}(1)=-t_{AB}^{JI}(1)=t_{BA}^{JI}(1), \tag{39b}$$

$$c_{IJ}^{KL}(0)=c_{IJ}^{LK}(0)=c_{JI}^{KL}(0)=c_{JI}^{LK}(0), \tag{39c}$$

$$c_{IJ}^{KL}(1)=-c_{IJ}^{LK}(1)=-c_{JI}^{KL}(1)=c_{JI}^{LK}(1). \tag{39d}$$

The symmetry properties of the intermediate doublet type T_3 amplitudes ($i=1-4$) are not that straightforward, except for permutations of the first two hole (particle) indices

$$(t_{ABC}^{IJK}(i))_{P_{AB}P_{IJ}}=(-1)^{P_{AB}S_{12}}(-1)^{P_{IJ}S^{12}}t_{ABC}^{IJK}(i). \tag{40a}$$

For other permutations the result is given by linear combination of doublet states (cf. Ref. 36)

$$t_{BCA}^{IJK}(i)=-\frac{1}{2}t_{ABC}^{IJK}(i)-(-1)^{S_{12}^j}\frac{\sqrt{3}}{2}t_{ABC}^{IJK}(j), \tag{40b}$$

$$t_{CAB}^{IJK}(i)=-\frac{1}{2}t_{ABC}^{IJK}(i)+(-1)^{S_{12}^j}\frac{\sqrt{3}}{2}t_{IJK}^{ABC}(j),$$

$$j=i+2(-1)^{S_{12}^i}, \tag{40c}$$

$$t_{ABC}^{JKI}(i)=-\frac{1}{2}t_{ABC}^{IJK}(i)-(-1)^{S_j^{12}}\frac{\sqrt{3}}{2}t_{ABC}^{IJK}(j), \tag{40d}$$

$$t_{CAB}^{IJK}(i)=-\frac{1}{2}t_{ABC}^{IJK}(i)+(-1)^{S_j^{12}}\frac{\sqrt{3}}{2}t_{ABC}^{IJK}(j),$$

$$j=i+(-1)^{S_i^{12}}. \tag{40e}$$

$S_i^{12}(S_{12}^i)$ denote $S^{12}(S_{12})$ corresponding to the ith configuration. Combining Eqs. (41a)–(41e) the result for any permutation of indices can be easily obtained. The quadruplet configuration fulfills the trivial permutation symmetry relation

$$(t_{ABC}^{IJK}(5))_P=(-1)^p t_{ABC}^{IJK}(5), \tag{40f}$$

where the subscript "P" means any permutation of the indices IJK; ABC and p is the parity of the permutation. Because of the symmetry properties, only the T_3 amplitudes

TABLE IV. Spin adapted intermediate effective interactions.[a]

$$\tilde{\mathscr{X}}^{IJ}_{KL}(i)=\tfrac{1}{2}\mathscr{X}^{MN}_{KL}(i)c^{IJ}_{MN}(i) \tag{IV.1}$$

$$\mathscr{G}^{IJ}_{RS}(i)=g^{IJ}_{RS}(i)+\tfrac{1}{2}\mathscr{V}^{MN}_{RS}(i)c^{IJ}_{MN}(i)+\tfrac{1}{2}g^{CD}_{RS}(i)\tau^{IJ}_{CD}(i)+(g^{DJ}_{RS}(i)t^I_D+g^{ID}_{RS}(i)t^J_D) \tag{IV.2}$$

$$\mathscr{F}^I_K=f^I_K+f^C_Kt^I_C+\tfrac{1}{4}(\mathscr{V}^{MN}_{KJ}(0)c^{IJ}_{MN}(0)+3\mathscr{V}^{MN}_{KJ}(1)c^{IJ}_{MN}(1)+g^{CD}_{KJ}(0)\tau^{IJ}_{CD}(0)+3g^{CD}_{KJ}(1)\tau^{IJ}_{CD}(1))+\tfrac{1}{2}(g^{IC}_{KJ}(0)+3g^{IC}_{KJ}(1))t^J_C \tag{IV.3}$$

$$\mathscr{G}^{CD}_{AB}(i)=g^{CD}_{AB}(i)+\tfrac{1}{2}g^{CD}_{KL}(i)\tau^{KL}_{AB}(i)-(g^{CD}_{LB}(i)t^L_A+g^{CD}_{AL}(i)t^L_B) \tag{IV.4}$$

$$\mathscr{F}^C_A=f^C_A-f^C_Kt^K_A-\tfrac{1}{4}(g^{CD}_{KL}(0)\tau^{KL}_{AD}(0)+3g^{CD}_{KL}(1)\tau^{KL}_{AD}(1))+\tfrac{1}{2}(g^{CD}_{AL}(0)+3g^{CD}_{AL}(1))t^L_D \tag{IV.5}$$

$$\mathscr{F}^C_K=f^C_K+\tfrac{1}{2}(g^{CD}_{KL}(0)+3g^{CD}_{KL}(1))t^L_D \tag{IV.6}$$

$$\mathscr{G}^{IC}_{AK}(i)\{w\}=g^{IC}_{AK}(i)+g^{DC}_{AK}(i)t^I_D-g^{IC}_{LK}(i)t^L_A+\frac{w}{2}(g^{CD}_{KL}(0)+3g^{CD}_{KL}(1))t^{LI}_{DA}-g^{CD}_{KL}(i)(wt^{LI}_{AD}+t^L_At^I_D) \tag{IV.7}$$

$$\begin{aligned}\mathscr{T}^{IJ}_{AK}(i)=\mathscr{G}^{IJ}_{AK}(i)+\sum_{P_{IJ}}(-1)^{iP_{IJ}}\{&\tfrac{1}{2}\mathscr{Z}^{CJ}_{LK}(t^{LI}_{CA}(0)+3t^{LI}_{CA}(1))\\&-\mathscr{Z}^{CJ}_{KL}t^{LI}_{CA}(i)\}-\mathscr{G}^{IJ}_{LK}(i)t^L_A\\&+\mathscr{F}^C_Kt^{IJ}_{AC}(i)+\frac{2}{3^i}g^{CD}_{KL}(t^{IJL}_{ACD}(3i+1)\\&+2it^{IJL}_{ACD}(3i+2))\end{aligned} \tag{IV.8}$$

$$\begin{aligned}\mathscr{T}^{IC}_{AB}(i)=g^{IC}_{AB}(i)+\tfrac{1}{2}\mathscr{Z}^{CI}_{KL}(i)\tau^{LK}_{AB}(i)+\sum_{P_{AB}}(-1)^{iP_{AB}}\{&\tfrac{1}{2}\mathscr{Z}^{DC}_{KB}(t^{KI}_{DA}(0)\\&+3t^{KI}_{DA}(1))-\mathscr{Z}^{CD}_{KB}t^{KI}_{DA}(i)\}-(\mathscr{Z}^{IC}_{AL}(i)t^L_B+\mathscr{Z}^{IC}_{LB}(i)t^L_A)\\&+g^{DC}_{AB}(i)t^I_D-\frac{2}{3^i}g^{CD}_{KL}(t^{IKL}_{ABD}(3i+1)+2it^{IKL}_{ABD}(3i+2))\end{aligned} \tag{IV.9}$$

$$\mathscr{Z}^{CI}_{KL}(i)=g^{CI}_{KL}(i)+g^{CD}_{KL}(i)t^I_D \tag{IV.10}$$

$$\mathscr{L}^{CD}_{KA}(i)=g^{CD}_{KA}(i)-g^{CD}_{KL}(i)t^L_A \tag{IV.11}$$

$$\mathscr{Z}^{IC}_{AK}(i)=g^{IC}_{AK}(i)+g^{DC}_{AK}(i)t^I_D \tag{IV.12}$$

[a] $i=0,1$ for intermediate singlet and triplet, respectively. $\tau^{IJ}_{AB}(i)=t^{IJ}_{AB}(i)+t^I_At^J_B+(-1)^it^J_At^I_B$. See also Tables I and III. In (IV.7) w may have the values $\frac{1}{2}$ or 1.

with $I\geqslant J$; $A\geqslant B$ or $I\geqslant J\geqslant K$; $A\geqslant B\geqslant C$ need to be calculated. As mentioned, for convenience we work with unnormalized amplitudes. Further, in Tables IV–V we also use

$$Y^{RS}_{PQ}=Y^{SR}_{QP}=\tfrac{1}{2}(Y^{RS}_{PQ}(0)+Y^{RS}_{PQ}(1)), \tag{41a}$$

$$Y^{RS}_{QP}=Y^{SR}_{PQ}=\tfrac{1}{2}(Y^{RS}_{PQ}(0)-Y^{RS}_{PQ}(1)) \tag{41b}$$

both for intermediates and amplitudes.

The spin "preadaptation" of the intermediate effective interactions yields what is given in Table IV and the final orthogonally spin adapted CCSDT-R12 equations are displayed in Table V, while the energy contribution (12) becomes

$$\begin{aligned}\Delta E=2\sum_{I,A}f^A_It^I_A+\sum_{S=0}^{1}(2S+1)&\times\Bigg\{\sum_{\substack{I\leqslant J\\A\leqslant B}}\left(\frac{1}{2}\right)^{\delta_{IJ}}\left(\frac{1}{2}\right)^{\delta_{AB}}g^{AB}_{IJ}(S)\tau^{IJ}_{AB}(S)\\&+\sum_{\substack{I\leqslant J\\K\leqslant L}}\left(\frac{1}{2}\right)^{\delta_{IJ}}\left(\frac{1}{2}\right)^{\delta_{KL}}\mathscr{V}^{KL}_{IJ}(S)c^{IJ}_{KL}(S)\Bigg\},\end{aligned} \tag{42}$$

where τ is defined in Table IV. With the use of analogy from Tables IV and V and Eq. (41) it is rather straightforward to express the fourth-order energy contributions from Eqs. (28) which we leave to the reader. Perhaps, it will be appropriate to give the energy contribution due to triples

$$\begin{aligned}\Delta E^{(4)}_T=+\sum_{i=1}^{5}(2S_i+1)\sum_{\substack{I\leqslant J\leqslant K\\A\leqslant B\leqslant C}}\left(\frac{1}{2}\right)^{\delta_{IJ}}\left(\frac{1}{2}\right)^{\delta_{AB}}t^{ABC^{(2)}}_{IJK}\\\times(i)D^{IJKABC}_{IJKABC}t^{ABC^{(2)}}_{IJK}(i).\end{aligned} \tag{43}$$

We are not going to analyse the equations for the T_1 and T_2 amplitudes as to the computational performance. Essentially, the same efficiency can be achieved as described in Ref. 40. However, due to the permutation symmetry properties of the amplitudes inherent to the theory no additional symmetrization is necessary to obtain the theoretical peak performance algorithm. The same is valid for triples. It is not only the fact that one needs to calculate just five linearly independent amplitudes, but the inherent symmetry makes it possible to improve our previous algorithm[28] quite significantly. Although this has been stressed already before,[36] a real comparison has not been made. It concerns mainly the most time consuming step, the contraction of T_3 amplitudes with *pp-pp* type intermediates. The number of floating point operations (FPO) in this case is reduced from $n_v^5n_0^3/2$ in Ref. 28 to $23n_v^5n_0^3/72$, i.e., by more than 25%. Similarly, the theoretical number of FPOs for the contraction of *hh-hh* type intermediates with T_3 amplitudes is reduced from $n_v^3n_0^5/2$ to $23n_v^3n_0^5/72$. Less theoretical efficiency improvement is achieved for the contraction of *ph-ph* intermediates with T_3, namely, $12n_v^4n_0^4$ vs $21n_v^4n_0^4/2$ (i.e., 12.5%).

VIII. CONCLUSIONS

In this paper we have presented the UHF and orthogonally spin adapted coupled cluster theory in which the interelectronic correlation cusp is treated via the inclusion of the interelectronic distance into the exponential ansatz. This is an extension of the use of the so-called R12 approach proposed in recent years by one of us together with Klopper and others.[2,3,12,13–17] A diagrammatic technique has been used to derive the CC-R12 equations with inclusion of single, double, triple, and the $\mathscr{R}$ excitation operators within the so-called standard approximation B. It has been shown that a great portion of the $\mathscr{R}$-containing diagrams vanish within the latter approximation and that the rest can be easily factorized. The method is fully connected, i.e., size extensive. Un-

TABLE V. Orthogonally spin adapted form of the CCSDT-R12 equations.[a]

$$\begin{aligned}
D^{IA}_{IA}t^{I}_{A}={}&f^{I}_{A}+\tilde{\mathscr{F}}^{C}_{A}t^{I}_{C}-\tilde{\mathscr{F}}^{I}_{K}t^{K}_{A}+\tfrac{1}{2}\,(g^{IC}_{AK}(0)+3g^{IC}_{AK}(1))t^{K}_{C}+\tfrac{1}{4}\,(g^{DC}_{AK}(0)t^{IK}_{DC}(0)+3g^{DC}_{AK}(1)t^{IK}_{DC}(1))-\tfrac{1}{4}\,(g^{CI}_{KL}(0)t^{KL}_{CA}(0)+3g^{CI}_{KL}(1)t^{KL}_{CA}(1))\\
&+\tfrac{1}{2}\,\mathscr{F}^{C}_{K}(t^{KI}_{CA}(0)+3t^{KI}_{CA}(i)+2t^{K}_{A}t^{I}_{C})+\tfrac{1}{2}\,g^{CD}_{KL}(2t^{IKL}_{ACD}(5)+t^{IKL}_{ACD}(1)+t^{IKL}_{ACD}(4))+\tfrac{1}{4}\,(\mathscr{V}^{KL}_{AM}(0)c^{IM}_{KL}(0)+3\mathscr{V}^{KL}_{AM}(1)c^{IM}_{KL}(1))
\end{aligned}\tag{V.1}$$

$$\begin{aligned}
D^{IJAB}_{IJAB}t^{IJ}_{AB}(i)={}&\sum_{P_{AI,BJ}}\,(\tilde{\mathscr{F}}^{C}_{A}t^{IJ}_{CB}(i)-\tilde{\mathscr{F}}^{I}_{K}t^{KJ}_{AB}(i))+\mathscr{G}^{IJ}_{AB}(i)+\tfrac{1}{2}\mathscr{G}^{IJ}_{KL}(i)\tau^{AB}_{KL}(i)+\sum_{P}\,(-1)^{iP}\{\tfrac{1}{2}(\mathscr{G}^{IC}_{AK}\{\tfrac{1}{2}\}(0)+3\mathscr{G}^{IC}_{AK}\{\tfrac{1}{2}\}(1))t^{KJ}_{CB}\\
&-\mathscr{G}^{IC}_{AK}\{\tfrac{1}{2}\}t^{KJ}_{BC}-\mathscr{G}^{CJ}_{AK}\{\tfrac{1}{2}\}t^{KI}_{BC}\}-(\mathscr{G}^{IJ}_{AK}(i)t^{K}_{B}+\mathscr{G}^{JI}_{BK}(i)t^{K}_{A})+\frac{2}{3^{i}}\,\mathscr{F}^{C}_{K}(t^{IJK}_{ABC}(4^{i})+2it^{IJK}_{ABC}(5))-\frac{2}{3^{i}}\sum_{P_{AI,BJ}}\,\{\mathscr{L}^{CI}_{KL}(t^{LJK}_{ABC}(4^{i})\\
&+2it^{LJK}_{ABC}(5))-\mathscr{L}^{CD}_{KA}(t^{IJK}_{DBC}(4^{i})+2i.t^{IJK}_{DBC}(5))\}\\
&\qquad i=0,1
\end{aligned}\tag{V.2}$$

$$\begin{aligned}
D^{IJKABC}_{IJKABC}t^{IJK}_{ABC}(i)={}&\tilde{\mathscr{F}}^{D}_{A}t^{IJK}_{DBC}(i)+\tilde{\mathscr{F}}^{D}_{B}t^{IJK}_{ADC}(i)+\tilde{\mathscr{F}}^{D}_{C}t^{IJK}_{ABD}(i)-\tilde{\mathscr{F}}^{I}_{L}t^{LJK}_{ABC}(i)-\tilde{\mathscr{F}}^{J}_{L}t^{ILK}_{ABC}(i)-\tilde{\mathscr{F}}^{K}_{L}t^{IJL}_{ABC}(i)+\Lambda^{ABC}_{IJK}(i)+\mathscr{G}^{IJ}_{LM}t^{LMK}_{ABC}(i)+\mathscr{G}^{IK}_{LM}t^{LJM}_{ABC}(i)\\
&+\mathscr{G}^{JK}_{LM}t^{ILM}_{ABC}(i)+\mathscr{G}^{DE}_{AB}t^{IJK}_{DEC}(i)+\mathscr{G}^{DE}_{AC}t^{IJK}_{DBE}(i)+\mathscr{G}^{DE}_{BC}t^{IJK}_{ADE}(i)-\mathscr{G}^{ID}_{LA}\{1\}t^{LJK}_{DBC}(i)-\mathscr{G}^{ID}_{LB}\{1\}t^{LJK}_{ADC}(i)-\mathscr{G}^{LD}_{LC}\{1\}t^{LJK}_{ABD}(i)\\
&-\mathscr{G}^{JD}_{LB}\{1\}t^{ILK}_{ADC}(i)-\mathscr{G}^{JD}_{LA}\{1\}t^{ILK}_{DBC}(i)-\mathscr{G}^{JD}_{LC}\{1\}t^{ILK}_{ABD}(i)-\mathscr{G}^{KD}_{LC}\{1\}t^{IJL}_{ABD}(i)-\mathscr{G}^{KD}_{LB}\{1\}t^{IJL}_{ADC}(i)-\mathscr{G}^{KD}_{LA}\{1\}t^{IJL}_{DBC}(i)\\
&\qquad i=1-5
\end{aligned}\tag{V.3}$$

$$\begin{aligned}
-\tfrac{1}{2}\mathscr{B}^{MN}_{KL}(i)c^{IJ}_{MN}(i)={}&-\mathscr{F}^{J}_{M}\tilde{\mathscr{X}}^{IM}_{KL}(i)-\mathscr{F}^{I}_{M}\tilde{\mathscr{X}}^{MJ}_{KL}(i)+(\mathscr{V}^{\dagger})^{IJ}_{KL}(i)+\tfrac{1}{2}\,\mathscr{G}^{IJ}_{MN}(i)\tilde{\mathscr{X}}^{MN}_{KL}(i)+\tfrac{1}{2}\,\mathscr{P}^{MN}_{KL}(i)c^{IJ}_{MN}(i)\\
&+\tfrac{1}{2}\,(\mathscr{V}^{\dagger})^{AB}_{KL}(i)\tau^{AB}_{IJ}(i)-\tfrac{1}{2}\,(\mathscr{Z}^{MN;J}_{KL;O}(i)c^{IO}_{MN}(i)+\mathscr{Z}^{MN;I}_{KL;O}(i)c^{OJ}_{MN}(i))\\
&-\tfrac{1}{2}\,(\mathscr{Z}^{MN;A}_{KL;O}(i)c^{IO}_{MN}(i)t^{J}_{A}+\mathscr{Z}^{MN;A}_{KL;O}(i)c^{OJ}_{MN}(i)t^{J}_{A})+\tfrac{1}{2}\,\mathscr{Z}^{MN;A}_{KL;O}(i)c^{IJ}_{MN}(i)t^{O}_{A}\\
&\qquad i=0,1
\end{aligned}\tag{V.4}$$

[a] See Tables III and IV. $\Lambda(i)$ is defined in Table VI. $P_{AI,BJ}$ means that AI is replaced by BJ.

like the originally suggested approach within perturbation theory but remedied later,[16] the present theory is invariant with respect to rotations of occupied orbitals. As a byproduct of CCSDT-R12 the MBPT(4)-R12 method is derived. The method presented here should improve the convergency of the total energy with respect to the saturation of the basis set from an error $\sim L^{-3}$ (conventional approach) to one $\sim L^{-7}$ where L is the maximum angular momentum included in the AO basis. It must be noted, however, that reliable calculations require relatively large basis sets for the low angular momenta l, since the standard approximation is based on the assumption that the basis is nearly saturated up to some minimum L value. As it has been shown previously, the minimum required L is related to the maximum l of the occupied AOs as $L=3l$

The inclusion of R12 terms into the CC equations requires only a minor increase of computational demands. Since the calculation of three types of two electron integrals needed for the R12 approaches is still just a minor part of the whole CC calculation, the total expected timings for conventional and R12 runs should be very similar. In particular, in the R12 approach the direct calculation of (at least) some contributions can be recommended, because typically $n_v \gg n_0$.

TABLE VI. Definition of $\Lambda(i)$ from Table V.[a]

$$\begin{aligned}
\Lambda^{IJK}_{ABC}(1)={}&-\tfrac{1}{2}\mathscr{T}^{IJK}_{CBA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{BCA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{ACB}-\tfrac{1}{2}\mathscr{T}^{IJK}_{CAB}+\mathscr{T}^{IJK}_{BAC}\\
&+\mathscr{T}^{IJK}_{ABC}
\end{aligned}\tag{VI.1a}$$

$$\Lambda^{IJK}_{ABC}(2)=\sqrt{3}(\tfrac{1}{2}\mathscr{T}^{IJK}_{CBA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{BCA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{ACB}+\tfrac{1}{2}\mathscr{T}^{IJK}_{CAB})\tag{VI.1b}$$

$$\Lambda^{IJK}_{ABC}(3)=\sqrt{3}(\tfrac{1}{2}\mathscr{T}^{IJK}_{CBA}+\tfrac{1}{2}\mathscr{T}^{IJK}_{BCA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{ACB}-\tfrac{1}{2}\mathscr{T}^{IJK}_{CAB})\tag{VI.1c}$$

$$\begin{aligned}
\Lambda^{IJK}_{ABC}(4)={}&\tfrac{1}{2}\mathscr{T}^{IJK}_{CBA}-\tfrac{1}{2}\mathscr{T}^{IJK}_{BCA}+\tfrac{1}{2}\mathscr{T}^{IJK}_{ACB}-\tfrac{1}{2}\mathscr{T}^{IJK}_{CAB}-\mathscr{T}^{IJK}_{BAC}\\
&+\mathscr{T}^{IJK}_{ABC}
\end{aligned}\tag{VI.1d}$$

$$\Lambda^{IJK}_{ABC}(5)=-\mathscr{T}^{IJK}_{CBA}+\mathscr{T}^{IJK}_{BCA}-\mathscr{T}^{IJK}_{ACB}+\mathscr{T}^{IJK}_{CAB}-\mathscr{T}^{IJK}_{BAC}+\mathscr{T}^{IJK}_{ABC}\tag{VI.1e}$$

$$\begin{aligned}
\mathscr{T}^{IJK}_{ABC}={}&\sum_{P_{IA,JB,KC}}(\mathscr{G}^{ID}_{AB}t^{JK}_{DC}-\mathscr{G}^{IJ}_{AL}t^{LK}_{BC})+\sum_{P_{IA,JB,KC}}\tfrac{2}{3}\mathscr{G}^{ID}_{AL}\{1\}\\
&\times(t^{LJK}_{DBC}(5)+t^{LJK}_{DBC}(4)+t^{LKJ}_{DCB}(4))
\end{aligned}\tag{VI.2}$$

[a] See Table IV and V. $P_{IA,JB,KC}$ means that the pair IA should be changed by JB and KC.

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APPENDIX A: ONE- AND TWO-ELECTRON OPERATORS AND THEIR CONTRACTED PRODUCTS

Let $\hat{f}$ be a one-electron operator and $\hat{A}$ a two-electron operator. They can be either represented in configuration space or in Fock space (n-electron operators should be invariant with respect to permutation of the particles)

$$\hat{f}=\sum_{k=1}^{n}\hat{f}(k)=f_{\mu}^{\nu}a_{\nu}^{\mu};\quad f_{\mu}^{\nu}=\langle\varphi_{\mu}(1)|\hat{f}(1)|\varphi_{\nu}(1)\rangle, \tag{A1a}$$

$$\hat{A}=\sum_{k<l=1}^{n}\hat{A}(k,l)=\frac{1}{2}A_{\mu\nu}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu};$$

$$A_{\mu\nu}^{\rho\sigma}=\langle\varphi_{\mu}(1)\varphi_{\nu}(2)|\hat{A}(1,2)|\varphi_{\rho}(1)\varphi_{\sigma}(2)\rangle, \tag{A1b}$$

$$\hat{A}(k,l)=A(l,k);\quad A_{\mu\nu}^{\rho\sigma}=A_{\nu\mu}^{\sigma\rho}. \tag{A1c}$$

A Fock space operator is regarded as equal to an operator in n-particle Hilbert space if they have the same matrix elements between arbitrary n-electron functions.

A product of two one-electron operators $\hat{f}$ and $\hat{g}$ is a sum of the normal product $:\hat{f}\hat{g}:$, which is a two-electron operator, and a contraction $(\hat{f}\hat{g})$ which is a one-electron operator

$$\hat{f}\hat{g}=:\hat{f}\hat{g}:+(\hat{f}\hat{g}), \tag{A2a}$$

$$:\hat{f}\hat{g}:=\sum_{k,l}{}'\hat{f}(k)\hat{g}(l)=2\sum_{k<l}\hat{f}(k)\hat{g}(l)=f_{\mu}^{\rho}g_{\nu}^{\sigma}a_{\rho\sigma}^{\mu\nu}, \tag{A2b}$$

$$(\hat{f}\hat{g})=\sum_{k}\hat{f}(k)\hat{g}(k)=f_{\mu}^{\nu}g_{\nu}^{\sigma}a_{\sigma}^{\mu}. \tag{A2c}$$

The generalization to products of more than two factors is evident.

One is also interested in commutators

$$[\hat{f},\hat{g}]=\sum_{k}\{\hat{f}(k)\hat{g}(k)-\hat{g}(k)\hat{f}(k)\}=(f_{\mu}^{\nu}g_{\nu}^{\sigma}-g_{\mu}^{\nu}f_{\nu}^{\sigma})a_{\sigma}^{\mu}. \tag{A2d}$$

Note the absence of a normal product term.

For a product or a commutator of a one-electron and a two-electron operator we get

$$\hat{f}\hat{A}=:\hat{f}\hat{A}:+(\hat{f}\hat{A}) \tag{A3a}$$

$$:\hat{f}\hat{A}:=\frac{1}{2}\sum_{k,l,m}{}'\hat{f}(k)\hat{A}(l,m)=\tfrac{1}{2}f_{\kappa}^{\lambda}A_{\mu\nu}^{\rho\sigma}a_{\lambda\rho\sigma}^{\kappa\mu\nu}. \tag{A3b}$$

A prime indicates that all labels are different

$$\begin{aligned}(\hat{f}\hat{A})&=\frac{1}{2}\sum_{k,l}{}'\hat{f}(k)\hat{A}(k,l)+\frac{1}{2}\sum_{k,l}{}'\hat{f}(l)\hat{A}(k,l)\\&=\sum_{k,l}{}'\hat{f}(k)\hat{A}(k,l)\\&=\frac{1}{2}f_{\kappa}^{\lambda}A_{\lambda\nu}^{\rho\sigma}a_{\rho\sigma}^{\kappa\nu}+\frac{1}{2}f_{\kappa}^{\lambda}A_{\mu\lambda}^{\rho\sigma}a_{\rho\sigma}^{\mu\kappa}=\frac{1}{2}(f_{\kappa}^{\lambda}A_{\lambda\nu}^{\rho\sigma}+f_{\nu}^{\lambda}A_{\kappa\lambda}^{\rho\sigma})a_{\rho\sigma}^{\kappa\nu}\\&=f_{\kappa}^{\lambda}A_{\lambda\nu}^{\rho\sigma}a_{\rho\sigma}^{\nu\kappa},\end{aligned} \tag{A3c}$$

$$\begin{aligned}[\hat{f},\hat{A}]&=\sum_{k,l}{}'\{\hat{f}(k)\hat{A}(k,l)-\hat{A}(k,l)\hat{f}(k)\}\\&=\frac{1}{2}(f_{\kappa}^{\lambda}A_{\lambda\nu}^{\rho\sigma}+f_{\nu}^{\lambda}A_{\kappa\lambda}^{\rho\sigma}-A_{\kappa\nu}^{\lambda\sigma}f_{\lambda}^{\rho}-A_{\kappa\nu}^{\rho\lambda}f_{\lambda}^{\sigma})a_{\rho\sigma}^{\kappa\nu}\\&=(f_{\kappa}^{\lambda}A_{\lambda\nu}^{\rho\sigma}-A_{\nu\kappa}^{\lambda\sigma}f_{\lambda}^{\rho})a_{\rho\sigma}^{\nu\kappa}.\end{aligned} \tag{A3d}$$

The product of two two-electron operators $\hat{A}$ and $\hat{B}$ involves both a single contraction $(\hat{A}\hat{B})$ and a double contraction $((\hat{A}\hat{B}))$. We skip the normal product

$$\begin{aligned}(\hat{A}\hat{B})&=\frac{1}{4}\sum_{k,l,m}{}'\{\hat{A}(k,l)\hat{B}(k,m)+\hat{A}(k,l)\hat{B}(l,m)\\&\quad+\hat{A}(k,l)\hat{B}(m,k)+\hat{A}(k,l)\hat{B}(m,l)\}\\&=\sum_{k,l,m}{}'\hat{A}(k,l)\hat{B}(k,m)\\&=\frac{1}{4}\{A_{\mu\nu}^{\kappa\lambda}B_{\kappa\tau}^{\rho\sigma}+A_{\mu\nu}^{\kappa\lambda}B_{\tau\kappa}^{\sigma\rho}+A_{\nu\mu}^{\lambda\kappa}B_{\kappa\tau}^{\rho\sigma}+A_{\nu\mu}^{\lambda\kappa}B_{\tau\kappa}^{\sigma\rho}\}a_{\rho\lambda\sigma}^{\mu\nu\tau}\\&=A_{\mu\nu}^{\kappa\lambda}B_{\kappa\tau}^{\rho\sigma}a_{\rho\lambda\sigma}^{\mu\nu\tau},\end{aligned} \tag{A4a}$$

$$\begin{aligned}((\hat{A}\hat{B}))&=\frac{1}{4}\sum_{k,l}{}'\{\hat{A}(k,l)\hat{B}(k,l)+\hat{A}(k,l)\hat{B}(l,k)\},\\&=\frac{1}{2}\sum_{k,l}{}'\hat{A}(k,l)\hat{B}(k,l),\\&=\frac{1}{4}(A_{\mu\nu}^{\kappa\lambda}B_{\kappa\lambda}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu}+A_{\mu\nu}^{\kappa\lambda}B_{\lambda\kappa}^{\rho\sigma}a_{\sigma\rho}^{\mu\nu}),\\&=\frac{1}{2}A_{\mu\nu}^{\kappa\lambda}B_{\kappa\lambda}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu}.\end{aligned} \tag{A4b}$$

In Fock space an alternative formulation of two-particle operators in terms of antisymmetrized matrix elements is possible, i.e., alternatively to Eq. (A.1b) we can write

$$\hat{A}=\tfrac{1}{4}\bar{A}_{\mu\nu}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu};\quad\bar{A}_{\mu\nu}^{\rho\sigma}=A_{\mu\nu}^{\rho\sigma}-A_{\mu\nu}^{\sigma\rho}. \tag{A5}$$

As alternatives to Eqs. (A3c), (A3d) and (A4) we then get

$$(\hat{f}\hat{A})=\tfrac{1}{2}f_{\kappa}^{\lambda}\bar{A}_{\lambda\nu}^{\rho\sigma}a_{\rho\sigma}^{\nu\kappa}, \tag{A6a}$$

$$[\hat{f},\hat{A}]=\tfrac{1}{2}(f_{\kappa}^{\lambda}\bar{A}_{\lambda\nu}^{\rho\sigma}-\bar{A}_{\nu\kappa}^{\lambda\sigma}f_{\lambda}^{\rho})a_{\rho\sigma}^{\nu\kappa}, \tag{A6b}$$

$$(\hat{A}\hat{B})=\tfrac{1}{4}\bar{A}_{\mu\nu}^{\kappa\nu}\bar{B}_{\kappa\tau}^{\rho\sigma}a_{\rho\lambda\sigma}^{\mu\nu\tau}, \tag{A7a}$$

$$((\hat{A}\hat{B}))=\tfrac{1}{8}\bar{A}_{\mu\nu}^{\kappa\lambda}\bar{B}_{\kappa\lambda}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu}. \tag{A7b}$$

Contractions involve—in the Fock space formulation—summations over infinite basis sets, which one wants to avoid. In configuration space contracted products are evaluated rather easily. If we write Eq. (A2c) as

$$(\hat{f}\hat{g})=\sum_{k}\hat{h}(k) \tag{A8a}$$

we have simply

$$\hat{h}(k)=\hat{f}(k)\hat{g}(k). \tag{A8b}$$

Similarly we get from Eq. (A4b)

$$((\hat{A}\hat{B}))=\hat{C}=\sum_{k<l}\hat{C}(k,l)=\frac{1}{2}C_{\mu\nu}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu}=\frac{1}{4}\bar{C}_{\mu\nu}^{\rho\sigma}a_{\rho\sigma}^{\mu\nu}; \tag{A9a}$$

$$\hat{C}(k,l)=\hat{A}(k,l)\hat{B}(k,l);$$

$$C^{\rho\sigma}_{\mu\nu}=A^{\kappa\lambda}_{\mu\nu}B^{\rho\sigma}_{\kappa\lambda}; \tag{A9b}$$

$$\bar{C}^{\rho\sigma}_{\mu\nu}=\tfrac{1}{2}\bar{A}^{\kappa\lambda}_{\mu\nu}\bar{B}^{\rho\sigma}_{\kappa\lambda}.$$

Consider the example that $A(k,l)=r_{kl}$, $B(k,l)=g_{kl}=r^{-1}_{kl}$, then in Hilbert space

$$((\hat{A}\hat{B}))=\sum_{k<l}1=\binom{n}{2} \tag{A10a}$$

and in Fock space

$$\begin{aligned}((\hat{A}\hat{B}))&=\tfrac{1}{2}r^{\kappa\lambda}_{\mu\nu}g^{\rho\sigma}_{\kappa\lambda}a^{\mu\nu}_{\rho\sigma}=\tfrac{1}{2}\langle\mu\nu|r|\kappa\lambda\rangle\langle\kappa\lambda|g|\rho\sigma\rangle a^{\mu\nu}_{\rho\sigma},\\ &=\tfrac{1}{2}\langle\mu\nu|rg|\rho\sigma\rangle a^{\mu\nu}_{\rho\sigma}\\ &=\tfrac{1}{2}\delta^{\rho}_{\mu}\delta^{\sigma}_{\nu}a^{\mu\nu}_{\rho\sigma}\\ &=\tfrac{1}{2}\,a^{\mu\nu}_{\mu\nu}\end{aligned} \tag{A10b}$$

The results are identical insofar as $a^{\mu\nu}_{\mu\nu}\Phi=n(n-1)\Phi$ for any n-electron functions Φ. Alternatively one gets from Eq. (A7b)

$$\begin{aligned}((\hat{A}\hat{B}))&=\tfrac{1}{8}\bar{r}^{\kappa\lambda}_{\mu\nu}\bar{g}^{\rho\sigma}_{\kappa\lambda}a^{\mu\nu}_{\rho\sigma}=\tfrac{1}{8}\langle\mu\nu-\nu\mu|r|\kappa\lambda\rangle\\ &\qquad\times\langle\kappa\lambda|g|\rho\sigma-\sigma\rho\rangle a^{\mu\nu}_{\rho\sigma},\\ &=\tfrac{1}{8}\langle\mu\nu-\nu\mu|\rho\sigma-\sigma\rho\rangle a^{\mu\nu}_{\rho\sigma}=\tfrac{1}{4}(a^{\mu\nu}_{\mu\nu}-a^{\mu\nu}_{\nu\mu})=\tfrac{1}{2}a^{\mu\nu}_{\mu\nu}.\end{aligned} \tag{A10c}$$

The singly contracted product of two two-electron operators (A4a) is a three-electron operator

$$(\hat{A}\hat{B})=\sum_{k<l<m}\hat{D}(k,l,m)=\frac{1}{6}D^{\rho\lambda\sigma}_{\mu\nu\tau}a^{\mu\nu\tau}_{\rho\lambda\sigma}, \tag{A11a}$$

$$\begin{aligned}\hat{D}(k,l,m)=\tfrac{3}{2}\{&\hat{A}(k,l)\hat{B}(k,m)+\hat{A}(k,l)\hat{B}(l,m)\\ &+\hat{A}(k,l)\hat{B}(m,k)+\hat{A}(k,l)\hat{B}(m,l)\}\end{aligned} \tag{A11b}$$

We also want to avoid operators of higher particle rank than two in configuration space and rather work in Fock space and try to simplify the summations over complete basis sets as needed in the last expression of Eq. (A4a).

We now assume that all operators that we consider are totally symmetric under the symmetry group of the respective Hamiltonian. This is the case for $\hat{A}(1,2)=r_{12}$ or $\hat{B}(1,2)=r^{-1}_{12}$, further for $\hat{f}$ the Fock operator. *We finally restrict our consideration to atoms*, then the AO basis $\{\varphi\}$ consists of subsets $\{\varphi_l\}$ characterized by some angular momentum quantum number l. Then

$$f^{\nu}_{\mu}=0 \quad \text{unless} \quad l(\mu)=l(\nu) \tag{A12}$$

consider the matrix element appearing in Eq. (A2c)

$$(fg)^{\sigma}_{\mu}=f^{\nu}_{\mu}g^{\sigma}_{\nu}=\langle\varphi_{\mu}|(\hat{f}\hat{g})|\varphi_{\sigma}\rangle. \tag{A13}$$

In view of Eq. (A12) and the same relation for g we see that only those term contribute to the sum over ν in Eq. (A13) for which

$$l(\mu)=l(\nu)=l(\sigma), \tag{A14}$$

i.e., only those matrix are nonzero for which $l(\sigma)=l(\mu)$, and in order to evaluate them in terms of a complete basis, the basis need only be saturated for this particular l value.

To satisfy this requirement to a good degree of approximation is much easier than to require that the basis is near complete, i.e., near saturated for *all l*. For this example the direct use of Eq. (A8) will usually be easier, nevertheless. This is not longer so, e.g., for Eq. (A4a).

APPENDIX B: PARTIAL WAVE EXPANSION OF OPERATORS AND THEIR CONTRACTED PRODUCTS

Totally symmetric local (multiplicative) two-electron operators can always be expanded as

$$\begin{aligned}\hat{A}(i,j)&=\sum_{l}a(r_i,r_j)P_l(\cos\vartheta_{ij})\\ &=4\pi\sum_{l}(2l+1)^{-1}a(r_i,r_j)\\ &\qquad\times\sum_{m=-l}^{l}Y^{m}_{l}(\vartheta_i,\varphi_i)Y^{m*}_{l}(\vartheta_j,\varphi_j).\end{aligned} \tag{B1}$$

For their matrix elements we therefore get

$$A^{\rho\sigma}_{\mu\nu}=\sum_{l=0}^{\infty}\langle\mu\nu|a|\rho\sigma\rangle_{\text{rad}}\frac{4\pi}{2l+1}\langle\mu|Y^{m}_{l}|\rho\rangle\langle\nu|Y^{m*}_{l}|\sigma\rangle, \tag{B2}$$

where rad indicates radial integration, while the other two brackets mean angular integration. The angular integration factorizes for each term. The triangular inequality implies that

$$|l(\mu)-l(\rho)|\leqslant l\leqslant l(\mu)+l(\rho), \tag{B3a}$$

$$|l(\nu)-l(\sigma)|\leqslant l\leqslant l(\nu)+l(\sigma). \tag{B3b}$$

Let

$$l_{\max}=\max\{l(\mu),l(\rho),l(\nu),l(\sigma)\}. \tag{B4a}$$

Then

$$l\leqslant 2l_{\max}, \tag{B4b}$$

i.e., the sum over l in Eq. (B2) is finite, provided that the basis functions φ_{μ}, etc., are angular-momentum eigenfunctions (what we have assumed). Moreover allowed values of $l(\mu)$, etc., are not arbitrary, but, e.g.,

$$l(\mu)\geqslant l(\rho)\Rightarrow l(\mu)\leqslant l(\nu)+l(\sigma)+l(\rho), \tag{B5}$$

i.e., one of the four values of $l(\mu),l(\rho),l(\nu),l(\sigma)$ is always smaller than or equal to the sum of the other three.

We now use this result to discuss contracted products of the type (A4a). Let

$$L=\min\{l(\lambda)+l(\mu)+l(\nu),l(\rho)+l(\sigma)+l(\tau)\}, \tag{B6a}$$

$$l(\kappa)\leqslant L, \tag{B6b}$$

i.e., the summation over κ for a specific term in Eq. (A4a) terminates at a finite l value. Hence the basis need be complete only up to this L value if one wants to evaluate this term by means of summation over the complete basis.

Let λ, μ, ν, ϱ, σ and τ all be occupied spin orbitals, usually labeled as i,j,k,... then

$$L=3\ \max\{l(i)\} \tag{B7}$$

i.e., the basis $\{\varphi_\kappa\}$ need only be saturated up to this L to be regarded as complete. If $l(i)=0$ for all i, then only $\kappa=0$ will contribute in the sum (A4a).

This makes single contractions rather easy.

The single contraction (A4a) is a special case of a chain contraction. Consider, e.g., the chain of two single contractions

$$A^{p\mu}_{qr}B^{s\nu}_{t\mu}C^{uv}_{w\nu}a^{qrtw}_{pvsu}. \tag{B8}$$

Here A is contracted with B by μ and B with C by ν. The generalization to longer chains is obvious. For fixed values of p,q,r,s,t,u,v,w the sums over ν and μ terminate at a finite l value both for μ and ν, due to the triangular inequality at each vertex.

If p,q,r,s,t,u,v,w all refer to occupied orbitals, we find

$$l(\mu)\leqslant L;\quad l(\nu)\leqslant L \tag{B9}$$

with L given by Eq. (B7). This holds essentially for all open-ended contractions. Nevertheless a slight change arises for a product of four factors

$$A^{\cdot\mu}_{\cdot\cdot}B^{\cdot\nu}_{\cdot\mu}C^{\cdot\rho}_{\cdot\nu}D^{\cdot\cdot}_{\cdot\rho}a^{\cdots}_{\cdots}. \tag{B10}$$

In analogy to Eq. (B9) we find

$$l(\mu)\leqslant L;\quad l(\rho)\leqslant L \tag{B11}$$

For $l(\nu)$ we only get

$$l(\nu)\leqslant l(\nu)+2\ \max\{l(i)\}\leqslant L', \tag{B12a}$$

$$L'=5\ \max\{l(i)\}. \tag{B12b}$$

Fortunately in the CCSDT-R12 no chains of more than three factors arise.

Let us now look at a cyclic contraction like

$$A^{\mu\nu}_{pq}B^{r\rho}_{\mu t}C^{uv}_{\nu\rho}a^{pqt}_{ruv}. \tag{B13a}$$

Here A is contracted with B and C, B with A and C, C with A and B. The l values of μ,ν,ρ are not restricted by any triangular inequalities and the summation limits for $l(\mu),l(\nu),l(\rho)$ become infinite.

In configuration space (B13a) means (except for a normalization factor)

$$\sum_{i<j<k} A(i,j)B(i,k)C(j,k). \tag{B13b}$$

We have a look at a matrix element of a term in Eq. (B13b) for the special case

$$A(i,j)=B(i,j)=C(i,j)=g_{ij}=r_{ij}^{-1}, \tag{B14}$$

$$K=\langle\varphi(1,2,3)|g_{12}g_{13}g_{23}|\varphi'(1,2,3)\rangle. \tag{B15}$$

For the sake of simplicity we assume that φ and φ' don't depend on the angular variables.

If we insert

$$g_{12}=\sum_{k=0}^{\infty} g_k(r_1,r_2)P_k(\cos\vartheta_{12}), \tag{B16a}$$

$$g_k=\frac{r_<^k}{r_>^{k+1}};\quad P_k(\cos\vartheta)=\frac{4\pi}{2k+1}\sum_{m=-k}^{k} Y_k^m(1)Y_k^{m*}(2) \tag{B16b}$$

then K becomes a sixfold sum (over three k values and three m values). The angular integrations are performed easily and in view of the orthogonality of the spherical harmonics we get

$$\begin{aligned}K&=\sum_k \frac{(4\pi)^3}{(2k+1)^2}\int \varphi^*(1,2,3)\varphi'(1,2,3)\\&\quad\times g_k(r_1,r_2)g_k(r_1,r_3)g_k(r_2,r_3)r_1^2r_2^2r_3^2\,dr_1\,dr_2\,dr_3\\&=\sum_k K_k.\end{aligned} \tag{B17}$$

The domain for the radial integration consists of six parts depending on whether $r_1\geqslant r_2\geqslant r_3$ or $r_1\geqslant r_3\geqslant r_2$, etc. It suffices to take one of these domains (e.g., the first) and multiply the result by 6

$$\begin{aligned}K_k&=6\,\frac{(4\pi)^3}{(2k+1)^2}\int_{r_1\geqslant r_2\geqslant r_3}\varphi^*\varphi'\,\frac{r_2^k}{r_1^{k+1}}\,\frac{r_3^k}{r_1^{k+1}}\,\frac{r_3^k}{r_2^{k+1}}\\&\quad\times r_1^2r_2^2r_3^2\,dr_1\,dr_2\,dr_3,\\&=6\,\frac{(4\pi)^3}{(2k+1)^2}\int_{r_1\geqslant r_2\geqslant r_3}\varphi^*\varphi' r_1^{-2k}r_2r_3^{2k+2}\,dr_1\,dr_2\,dr_3.\end{aligned} \tag{B18}$$

For large k the integrand strongly peaks at $r_1=r_2=r_3$.

While the factor involving r_1,r_2,r_3 varies strongly in the neighbourhood of $r_1=r_2=r_3$, the factor $\varphi\varphi'$ varies weakly. One can expand $\varphi\varphi'$ in a Taylor series

$$\begin{aligned}\varphi^*\varphi'&=\varphi^*(r_1,r_1,r_1)\varphi'(r_1,r_1,r_1)+(r_2-r_1)\,\frac{\partial(\varphi^*\varphi')}{\partial r_2}\\&\quad+(r_3-r_1)\,\frac{\partial(\varphi^*\varphi')}{\partial r_3}+\cdots.\end{aligned} \tag{B19}$$

If we take only the first term in Eq. (B19), we can easily integrate first r_3 from 0 to r_2, afterwards r_2 from 0 to r_1 and finally r_1 from 0 to ∞, such that

$$
\begin{aligned}
K_k &= 6\,\frac{(4\pi)^3}{(2k+1)^2}\int_{r_1\geqslant r_2}\varphi^*(1,1,1)\varphi'(1,1,1)\,\frac{r_1^{-2k}}{2k+3}\,r_2^{2k+4}\,dr_1\,dr_2\\
&= \frac{6(4\pi)^3}{(2k+1)^2(2k+3)(2k+5)}\int\varphi^*(1,1,1)\varphi'(1,1,1)r_1^5\,dr_1\\
&= \frac{3(2\pi)^3}{(k+\frac{1}{2})^4}\int\varphi^*(1,1,1)\varphi'(1,1,1)r_1^5\,dr_1+O([k+\tfrac{1}{2}]^{-5}).
\end{aligned}
\tag{B20}
$$

The angular integration has introduced a factor $(k+\frac{1}{2})^{-2}$, the radial integration another factor $(k+\frac{1}{2})^{-2}$ such that an overall $(k+\frac{1}{2})^{-4}$ dependence of the partial wave contribution K_k to the integral K results.

Let us now look at the contributions of the second and third as well as the higher order terms in Eq. (B19). In the integrand $\varphi^*\varphi'$ is replaced by some derivative of $\varphi^*\varphi'$ and there is an extra factor such as (r_2-r_1). For the particular factor (r_2-r_1) we get as counterpart of Eq. (B20)

$$
\begin{aligned}
&6\,\frac{(4\pi)^3}{(2k+1)^2}\int_{r_1\geqslant r_2\geqslant r_3}\frac{\partial(\varphi^*\varphi')}{\partial r_2}\,[r_1^{-2k}r_2^2r_3^{2k+2}-r_1^{-2k+1}r_2r_3^{2k+2}]dr_1\,dr_2\,dr_3\\
&=6\,\frac{(4\pi)^3}{(2k+1)^2}\int_{r_1\geqslant r_2}\frac{\partial(\varphi^*\varphi')}{\partial r_2}\left[\frac{r_1^{-2k}}{2k+3}\,r_2^{2k+5}-\frac{r_1^{-2k+1}}{2k+3}\,r_2^{2k+4}\right]dr_1\,dr_2\\
&=6\,\frac{(4\pi)^3}{(2k+1)^2}\int\frac{\partial(\varphi^*\varphi')}{\partial r_2}\,r_1^6\left[\frac{1}{(2k+3)(2k+6)}-\frac{1}{(2k+3)(2k+5)}\right]dr_1\\
&=-6\,\frac{(4\pi)^3}{(2k+1)^2(2k+3)(2k+5)(2k+6)}\int\frac{\partial(\varphi^*\varphi')}{\partial r_2}\,r_1^6\,dr_1\\
&=O[(k+\tfrac{1}{2})^{-5}].
\end{aligned}
\tag{B21}
$$

This means that the second and higher terms of the Taylor expansion (B19) contribute to higher order in $(k+\frac{1}{2})^{-1}$ than $(k+\frac{1}{2})^{-4}$. To get the leading term in the $(k+\frac{1}{2})^{-1}$ expansion it is sufficient to take the leading term in Eq. (B19).

Before we discuss the generalization of this result to the case that φ and φ' depend on the angular variables, we must make two remarks.

(a) It may happen that $\varphi(1,1,1)$ vanishes. In this case the term $O([k+\frac{1}{2}]^{-4})$ in the $(k+\frac{1}{2})^{-1}$ expansion vanishes. Then higher terms in expansion (B19) have to be considered and K_k starts with a term of higher order in $(k+\frac{1}{2})^{-1}$ than $(k+\frac{1}{2})^{-4}$.

(b) Usually we will not be interested in a product with three g_{ij} factors, rather with two r_{ij} and one g_{ij} factors. It is relatively easy to see that replacement of g_{12} by r_{12}, i.e., of $r_<^k/r_>^{k+1}$ by

$$
r_k=\frac{1}{2k+1}\,\frac{r_<^{k+3}}{r_>^{k+1}}-\frac{1}{2k-1}\,\frac{r_<^k}{r_>^{k-1}}
\tag{B22}
$$

introduces two more $(k+\frac{1}{2})^{-1}$ factors in the final result. One of these is explicitly present in Eq. (B22). The other arises because due to the difference in sign of the two terms in Eq. (B22) the leading terms in the integral cancel. So for the integral

$$
K'=\langle\varphi(1,2,3)|r_{12}g_{13}r_{23}|\varphi'(1,2,3)\rangle
\tag{B23}
$$

the leading term in the partial wave expansion goes at least as $(k+\frac{1}{2})^{-8}$ and can be neglected in the standard approximation.

Let us now allow that φ and φ' depend on the angular variables, as

$$
\begin{aligned}
\varphi^*=f^*(r_1,r_2,r_3)Y_{l_1}^{m_1*}(\vartheta_1,\varphi_1)Y_{l_2}^{m_2*}&\\
\times(\rho_2,\varphi_2)Y_{l-3}^{m_3*}(\vartheta_3,\varphi_3),&
\end{aligned}
\tag{B24a}
$$

$$
\varphi'=f'(r_1,r_2,r_3)Y_{l_4}^{m_4}(\vartheta_1,\varphi_1)Y_{l_5}^{m_5}(\vartheta_2,\varphi_2)Y_{l_6}^{m_6}(\vartheta_3,\varphi_3).
\tag{B24b}
$$

One expands

$$
Y_{l_1}^{m_1^*}(\vartheta_1,\varphi_1)Y_{l_4}^{m_4}(\vartheta_1,\varphi_1)
=\sum_{L_1}c(l_1,l_4,L_1,-m_1,m_4,M_1)Y_{L_1}^{M_1}(\vartheta_1,\varphi_1)
\tag{B25a}
$$

such that

$$
\begin{aligned}
\varphi^*\varphi=\sum_{L_1,L_2,L_3}F_L(r_1,r_2,r_3)Y_{L_1}^{M_1}(\vartheta_1\varphi_1)&\\
\times Y_{L_2}^{M_2}(\vartheta_2,\varphi_2)Y_{L_3}^{M_3}(\vartheta_3,\varphi_3)&
\end{aligned}
\tag{B25b}
$$

where F_2 depends on L_1,L_2,L_3 and where the summation limits over L_1,L_2,L_3 are determined by the triangular inequality in Eq. (B25a).

We can insert Eq. (B25b) into Eq. (B15), but we consider only a single term in the sum (B25b). The angular integration is now not trivial as in Eq. (B17), but we rather get a sixfold sum over k,k',k'',m,m',m''. One term in this sum is

$$6\,\frac{(4\pi)^3}{(2k+1)^3}\int_{r_1\geqslant r_2\geqslant r_3} F_L\,\frac{r_2^k}{r_1^{k+1}}\,\frac{r_3^{k'}}{r_1^{k'+1}}\,\frac{r_3^{k''}}{r_2^{k''+1}}\,r_1^2r_2^2r_3^2$$
$$\times dr_1\,dr_2\,dr_3\int Y_{L_1}^{M_1}(\vartheta_1,\varphi_1)Y_k^{m*}(\vartheta_1,\varphi_1)Y_{k'}^{m'}\,d\omega_1$$
$$\times(\rho_1,\varphi_1)dw_1\int Y_{L_2}^{M_2}(2)Y_{k'}^{m'}{}^*(2)Y_{k'}^{m''}(2)d\omega_2$$
$$\times\int Y_{L_3}^{M_3}(3)Y_{k''}^{m''}{}^*(3)Y_k^m(3)d\omega_3\,. \tag{B26}$$

The radial integration in Eq. (B26) leads to

$$(k'+k''+3)^{-1}(k+k'+5)^{-1}\int r_1^5F_L(r_1,r_1,r_1)dr_1 \tag{B27}$$

while the angular integrals can be expressed in terms of $3j$ symbols. It is recommended to define

$$p=k'-k;\quad q=k''-k \tag{B28}$$

where p and q have finite limits due to triangular inequalities, while k is unbounded. One can then use asymptotic expansions of $3j$ symbols for large k. A closed summation over the leading term is then possible and the final result is that K_k goes as $(k+\frac{1}{2})^{-4}$ as in Eq. (B20).

The generalization to a cyclic product of four operators is straightforward. Instead of Eq. (B15) we now have

$$K=\langle\varphi(1,2,3,4)|g_{12}g_{23}g_{34}g_{41}|\varphi'(1,2,3,4)\rangle. \tag{B29}$$

We assume again that φ and φ' do not depend on the angular variables.

We insert Eq. (B16) and K becomes an eightfold sum (over four k values and four m values). We can then perform the angular integration and get in view of the orthogonality of the spherical harmonics

$$K=\sum_k\frac{(4\pi)^4}{(2k+1)^3}\int\varphi^*\varphi'g_k(r_1,r_2)g_k(r_2,r_3)g_k(r_3,r_4)$$
$$\times g_k(r_4,r_1)r_1^2r_2^2r_3^2r_4^2\,dr_1\,dr_2\,dr_3\,dr_4$$
$$=\sum_k K_k, \tag{B30}$$

$$K_k=24\,\frac{(4\pi)^4}{(2k+1)^3}\int\varphi^*\varphi'\,\frac{r_2^k}{r_1^{k+1}}\,\frac{r_3^k}{r_2^{k+1}}\,\frac{r_4^k}{r_3^{k+1}}\,\frac{r_4^k}{r_1^{k+1}}$$
$$\times r_1^2r_2^2r_3^2r_4^2\,dr_1\,dr_2\,dr_3\,dr_4,$$
$$=24\,\frac{(4\pi)^4}{(2k+1)^3}\int\varphi^*\varphi' r_1^{-2k}r_2r_3r_4^{2k+2}\,dr_1\,dr_2\,dr_3\,dr_4. \tag{B31}$$

(The factor 24 comes from the 24 possible permutations of r_1,r_2,r_3,r_4). For large k this strongly peaks at $r_1=r_2=r_3=r_4$ and we can replace $\varphi(1,2,3,4)$ by $\varphi(1,1,1,1)$. We can then integrate over r_4 from 0 to r_3, subsequently over r_3 from 0 to r_2, over r_2 from 0 to r_1 and finally over r_1 from 0 to ∞, such that

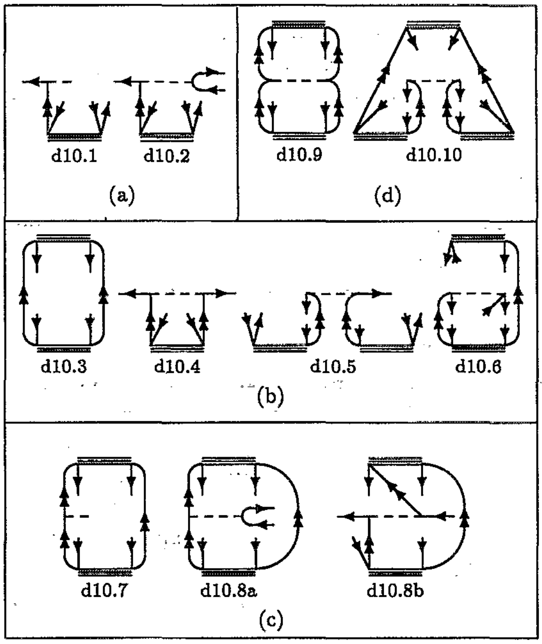

FIG. 10. Basic diagrammatic fragments that include one (a), two (b), three (c), and fourfold (d) summations over complete basis. For d10.8 we distinguish between two Goldstone type diagrams, as it is essential for the standard approximation.

$$K_k=24\,\frac{(4\pi)^4}{(2k+1)^3}\int\varphi^*(1,1,1,1)\varphi'(1,1,1,1)$$
$$\times\frac{r_1^7\,dr_1}{(2k+3)(2k+5)(2k+7)},$$
$$=6(2\pi)^4(k+\tfrac{1}{2})^{-6}\int\varphi^*(1,1,1,1)\varphi'(1,1,1,1)r_1^7\,dr_1$$
$$+O(k+\tfrac{1}{2})^{-7}. \tag{B32}$$

The essential result, namely the $(k+\frac{1}{2})^{-6}$ dependence remains valid, if φ^* and φ' depend on the angular variables. Replacement of a factor g_{12} by r_{12} introduces an additional factor $(k+\frac{1}{2})^{-2}$, such that for the expression, in which we are actually interested, namely,

$$\langle\varphi|r_{12}g_{23}r_{34}r_{41}|\varphi\rangle$$

the leading term goes as $(k+\frac{1}{2})^{-12}$. If $\varphi(r_1,r_2,r_3)=0$ the leading term has at least another additional factor $(k+\frac{1}{2})^{-1}$.

APPENDIX C: DIAGRAMS WITH A SINGLE CONTRACTION OVER A COMPLETE BASIS

On Fig. 10 the diagram fragments involving single double and higher contractions are collected. With single contraction they are of the following types:

$$d10.1{:}f_p^\alpha\bar{R}_{ab}^{ij}\quad d10.2{:}\bar{g}_{qr}^{\alpha p}\bar{R}_{ab}^{ij}. \tag{C1}$$

The matrix elements f_p^α vanish unless $l(\alpha)=l(p)$. Since the basis—to which p belongs—is chosen so that it is saturated up to some l value L, also $l(\alpha)\leqslant L$, hence the sum over the complete basis can be replaced by one over the given basis, i.e.,

$$f_p^\alpha \bar{R}^{ij}_{\alpha b}=f_p^\alpha \bar{r}^{ij}_{\alpha b}-f_p^a \bar{r}^{ij}_{ab}=0 \tag{C2}$$

and diagram fragments of type (d10.1) can be neglected in the standard approximation (A or B).

We come now to the fragment d10.2

$$\bar{g}^{\alpha p}_{qr}\bar{R}^{ij}_{\alpha b}=\bar{g}^{\alpha p}_{qr}\bar{r}^{ij}_{\alpha b}-\bar{g}^{ap}_{qr}\bar{r}^{ij}_{ab}. \tag{C3}$$

The simplest case is realized if the orbital φ_b has an angular momentum $l(b)$ that agrees with an l of the occupied MOs. Then $l(\alpha)\leqslant L$. In order to satisfy the conditions for the standard approximation we choose the basis $\{a\}$ such that it is near saturated up to $l(a)=L$. Then the two sums on the r.h.s. of Eq. (C3) terminate at the same l and the result is zero within the standard approximation. The same argument holds if the three labels $p,q,r,$ on $\bar{g}$ correspond to occupied MOs or MOs with the same l as occupied MOs.

Another simple case is realized if $l(i)=l(j)=0$ and all other l arbitrary. In this case $l(\alpha)=l(b)$ and if the basis $\{a\}$ is chosen such that is saturated up to $l(a)=L$, the two terms in Eq. (C3) cancel.

For $l(i)\neq l(j)$ and $l(b)<L$ sufficiently large, expression (C3) does no longer vanish under the condition of the standard approximation, but its partial-wave contributions vanish with sufficiently high power of $[l(\alpha)+\frac{1}{2}]^{-1}$ such that Eq. (C3) can be neglected even then.

APPENDIX D: DIAGRAMS WITH DOUBLE CONTRACTIONS OVER A COMPLETE BASIS

Let us first look at double contractions between a pair of vertices, i.e. (see Fig. 10)

$$d10.3{:}\mathscr{X}^{kl}_{ij}=\tfrac{1}{2}\bar{R}^{\alpha\beta}_{ij}\bar{R}^{kl}_{\alpha\beta};\quad d10.4{:}\mathscr{Y}^{ij}_{pq}=\tfrac{1}{2}\bar{g}^{\alpha\beta}_{pq}\bar{R}^{ij}_{\alpha\beta}. \tag{D1}$$

We first show that in both cases the summation over (α,β) can be replaced by a sum over the complete set (μ,ν)

$$\bar{g}^{\alpha\beta}_{pq}\bar{R}^{ij}_{\alpha\beta}=\bar{g}^{\alpha\beta}_{pq}\bar{r}^{ij}_{\alpha\beta}-\bar{g}^{ab}_{pq}\bar{r}^{ij}_{ab}, \tag{D2}$$

$$\bar{g}^{\alpha\beta}_{pq}\bar{r}^{ij}_{\alpha\beta}=\bar{g}^{\mu\nu}_{pq}\bar{r}^{ij}_{\mu\nu}-\bar{g}^{k\nu}_{pq}\bar{r}^{ij}_{k\nu}-\bar{g}^{\mu l}_{pq}\bar{r}^{ij}_{\mu l}+\bar{g}^{kl}_{pq}\bar{r}^{ij}_{kl}, \tag{D3a}$$

$$\bar{g}^{ab}_{pq}\bar{r}^{ij}_{ab}=\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs}-\bar{g}^{ks}_{pq}\bar{r}^{ij}_{ks}-\bar{g}^{rl}_{pq}\bar{r}^{ij}_{rl}+\bar{g}^{kl}_{pq}\bar{r}^{ij}_{kl}. \tag{D3b}$$

Since in view of Appendix C

$$\bar{g}^{k\nu}_{pq}\bar{r}^{ij}_{k\nu}\overset{\text{s.a.}}{=}\bar{g}^{ks}_{pq}\bar{r}^{ij}_{ks}. \tag{D4}$$

It follows that

$$\bar{g}^{\alpha\beta}_{pq}\bar{R}^{ij}_{\alpha\beta}\overset{\text{s.a.}}{=}\bar{g}^{\mu\nu}_{pq}\bar{R}^{ij}_{\mu\nu} \tag{D5a}$$

and analogously

$$\bar{R}^{\alpha\beta}_{ij}\bar{R}^{kl}_{\alpha\beta}\overset{\text{s.a.}}{=}\bar{R}^{\mu\nu}_{ij}\bar{R}^{kl}_{\mu\nu}. \tag{D5b}$$

We can use results of Appendix A and get

$$\begin{aligned}\mathscr{Y}^{ij}_{pq}&=\tfrac{1}{2}\bar{g}^{\mu\nu}_{pq}\bar{R}^{ij}_{\mu\nu}=\tfrac{1}{2}(\bar{g}^{\mu\nu}_{pq}\bar{r}^{ij}_{\mu\nu}-\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs})=(\overline{gr})^{ij}_{pq}-\tfrac{1}{2}\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs}\\&=\delta^{ij}_{pq}-\tfrac{1}{2}\bar{g}^{rs}_{pq}\bar{r}^{ij}_{rs},\end{aligned} \tag{D6a}$$

$$\mathscr{X}^{kl}_{ij}=\tfrac{1}{2}\bar{R}^{\mu\nu}_{ij}\bar{R}^{kl}_{\mu\nu}=(\bar{r}^2)^{kl}_{ij}-\tfrac{1}{2}\bar{r}^{rs}_{ij}\bar{r}^{kl}_{rs};\quad \delta^{ij}_{pq}=\delta^{i}_{p}\delta^{j}_{q}-\delta^{i}_{q}\delta^{j}_{p}. \tag{D6b}$$

The adjoint of d10.4 yields

$$(\mathscr{Y}^{\dagger})^{pq}_{ij}=\tfrac{1}{2}\bar{R}^{\alpha\beta}_{ij}\bar{g}^{pq}_{\alpha\beta}\overset{\text{s.a.}}{=}\delta^{pq}_{ij}-\tfrac{1}{2}\bar{r}^{rs}_{ij}\bar{g}^{pq}_{rs}. \tag{D6c}$$

We must next consider double contractions involving three vertices (see Fig. 10)

$$d10.5{:}\bar{g}^{\alpha\beta}_{pq}\bar{R}^{ij}_{a\beta}\bar{R}^{kl}_{\alpha c},\quad d10.6{:}\bar{R}^{\alpha b}_{ij}\bar{g}^{c\beta}_{kl}\bar{R}^{mn}_{\alpha\beta}. \tag{D7}$$

Let us consider the special case

$$l(i)=l(j)=l(k)=l(l)=0 \tag{D8}$$

then

$$l(\beta)=l(a);\quad l(\alpha)=l(c)\quad \text{for } d10.5, \tag{D9a}$$

$$l(\beta)=l(c);\quad l(\alpha)=l(b)\quad \text{for } d10.6, \tag{D9b}$$

saturating the basis $l(\alpha)$ up to L causes the contracted products (D7) to vanish. If condition (D8) is not satisfied, these contributions decay at least fast enough with $(l(\alpha)+\frac{1}{2})^{-1}$ and $(l(\beta)+\frac{1}{2})^{-1}$, expression (D7) will hence be neglected in the standard approximation (A and B).

APPENDIX E: DIAGRAMS WITH TRIPLE CONTRACTIONS OVER A COMPLETE BASIS INVOLVING THE FOCK OPERATOR

Very important are expressions like d10.7 on Fig. 10

$$\begin{aligned}\mathscr{B}^{kl}_{ij}&=\bar{R}^{\alpha\beta}_{ij}f^{\gamma}_{\beta}\bar{R}^{kl}_{\alpha\gamma}\\&=\bar{r}^{\alpha\beta}_{ij}f^{\gamma}_{\beta}\bar{r}^{kl}_{\alpha\gamma}-\bar{r}^{ab}_{ij}f^{\gamma}_{b}\bar{r}^{kl}_{a\gamma}-\bar{r}^{a\beta}_{ij}f^{c}_{\beta}\bar{r}^{kl}_{ac}+\bar{r}^{ab}_{ij}f^{c}_{b}\bar{r}^{kl}_{ac}\\&\overset{\text{s.a.}}{=}\bar{r}^{\mu\nu}_{ij}f^{\kappa}_{\nu}\bar{r}^{kl}_{\mu\kappa}-\bar{r}^{pq}_{ij}f^{\kappa}_{q}\bar{r}^{kl}_{p\kappa}-\bar{r}^{p\nu}_{ij}f^{r}_{\nu}\bar{r}^{kl}_{pr}+\bar{r}^{pq}_{ij}f^{r}_{q}\bar{r}^{kl}_{pr}.\end{aligned} \tag{E1}$$

For their evaluation we first make a few statements. Let

$$\hat{f}=f^{\kappa}_{\lambda}a^{\lambda}_{\kappa};\quad \hat{r}_{12}=\tfrac{1}{2}r^{\mu\nu}_{\rho\sigma}a^{\rho\sigma}_{\mu\nu} \tag{E2}$$

then (see Appendix A)

$$[\hat{f},\hat{r}_{12}]=\tfrac{1}{2}[f,r_{12}]^{\mu\nu}_{\rho\sigma}a^{\rho\sigma}_{\mu\nu} \tag{E3a}$$

$$[f,r_{12}]^{\mu\nu}_{\rho\sigma}=f^{\tau}_{\rho}r^{\mu\nu}_{\tau\sigma}+f^{\tau}_{\sigma}r^{\mu\nu}_{\rho\tau}-r^{\tau\nu}_{\rho\sigma}f^{\mu}_{\tau}-r^{\mu\tau}_{\rho\sigma}f^{\nu}_{\tau}. \tag{E3b}$$

On the other hand,[12]

$$[\hat{f},\hat{r}_{12}]=-2\bar{g}_{12}+2\hat{u}_{12}-[\hat{K},\hat{r}_{12}], \tag{E4a}$$

$$\begin{aligned}[f,r_{12}]^{\mu\nu}_{\rho\sigma}=&-2g^{\mu\nu}_{\rho\sigma}+2u^{\mu\nu}_{\rho\sigma}+r^{\mu\tau}_{\rho\sigma}g^{i\nu}_{\tau i}+r^{\tau\nu}_{\rho\sigma}g^{i\mu}_{\tau i}-g^{i\tau}_{\sigma i}r^{\mu\nu}_{\rho\tau}\\&-g^{i\tau}_{\rho i}r^{\mu\nu}_{\tau\sigma},\end{aligned} \tag{E4b}$$

$$\hat{u}_{12}=-\frac{1}{2r_{12}}\,\mathbf{r}_{12}\cdot(\boldsymbol{\nabla}_1-\boldsymbol{\nabla}_2) \tag{E4c}$$

We further note that

$$\bar{A}^{\mu\nu}_{ij}f^{\kappa}_{\nu}\bar{B}^{kl}_{\mu\kappa}=\tfrac{1}{2}(\overline{Af}\,)^{\mu\kappa}_{ij}\bar{B}^{kl}_{\mu\kappa}=\tfrac{1}{2}\bar{A}^{\mu\nu}_{ij}(\overline{fB})^{kl}_{\mu\nu}, \tag{E5a}$$

where $(\overline{Af}\,)$ and $(\overline{fB})$ mean the contracted part of the antisymmetrized product of A and f or f and B, respectively,

$$(\overline{Af}\,)^{\mu\kappa}_{ij}=\bar{A}^{\mu\nu}_{ij}f^{\kappa}_{\nu}-\bar{A}^{\kappa\nu}_{ij}f^{\mu}_{\nu}, \tag{E5b}$$

$$(\overline{fB})^{kl}_{\mu\nu}=f^{\kappa}_{\nu}\bar{B}^{kl}_{\mu\kappa}-f^{\kappa}_{\mu}\bar{B}^{kl}_{\kappa\nu}. \tag{E5c}$$

For the evaluation of Eq. (E1) we proceed first as in Ref. 12, i.e., we assume the extended Brillouin theorem according to which f^{α}_{b} vanishes if b corresponds to the given basis and α to an element of the complete basis not contained in the given basis. This means we can replace f^{α}_{b} by f^{a}_{b} or vice versa. This allows us to rewrite Eq. (E1) in two alternative ways

$$\mathscr{B}^{kl}_{ij}\overset{\text{s.a.}}{=}\bar{r}^{\mu\nu}_{ij}f^{\kappa}_{\nu}\bar{r}^{kl}_{\mu\kappa}-\bar{r}^{pq}_{ij}f^{\kappa}_{q}\bar{r}^{kl}_{p\kappa}=\tfrac{1}{2}\bar{r}^{\mu\nu}_{ij}(\overline{fr})^{kl}_{\mu\nu}-\tfrac{1}{2}\bar{r}^{pq}_{ij}(\overline{fr})^{kl}_{pq}, \tag{E6a}$$

$$\mathscr{B}^{kl}_{ij}\overset{\text{s.a.}}{=}\bar{r}^{\mu\nu}_{ij}f^{\kappa}_{\nu}\bar{r}^{kl}_{\mu\kappa}-\bar{r}^{p\nu}_{ij}f^{r}_{\nu}\bar{r}^{kl}_{pr}=\tfrac{1}{2}(\overline{rf}\,)^{\mu\kappa}_{ij}\bar{r}^{kl}_{\mu\kappa}-\tfrac{1}{2}(\overline{rf}\,)^{p\nu}_{ij}\bar{r}^{kl}_{p\nu}. \tag{E6b}$$

In Eq. (E6a) we have assumed that the third and fourth terms of Eq. (E1) cancel, in Eq. (E6b) that the second and fourth terms cancel. We shall see later that one can also evaluate Eq. (E6) without assuming the extended Brillouin condition.

For the further evaluation of Eq. (E6a) we use

$$\mathscr{B}^{kl}_{ij}\overset{\text{s.a.}}{=}\tfrac{1}{2}\,\bar{r}^{\mu\nu}_{ij}\{[\overline{f,r}]^{kl}_{\mu\nu}+\bar{r}^{\kappa l}_{\mu\nu}f^{k}_{\kappa}+\bar{r}^{k\kappa}_{\mu\nu}f^{l}_{\kappa}\}-\tfrac{1}{2}\,\bar{r}^{pq}_{ij}\{[\overline{f,r}]^{kl}_{pq}$$
$$+\bar{r}^{\kappa l}_{pq}f^{k}_{\kappa}+\bar{r}^{k\kappa}_{pq}f^{l}_{\kappa}\} \tag{E7}$$

and note that f^{k}_{κ} vanishes unless κ is an occupied MO (ordinary Brillouin theorem) i.e., unless $f^{k}_{\kappa}=f^{k}_{m}$. We insert Eq. (E4) and get

$$\mathscr{B}^{kl}_{ij}=\tfrac{1}{2}\bar{r}^{\mu\nu}_{ij}\{-2\hat{g}^{kl}_{\mu\nu}+2\bar{u}^{kl}_{\mu\nu}+\bar{r}^{k\kappa}_{\mu\nu}g^{ml}_{\kappa m}+\bar{r}^{\kappa l}_{\mu\nu}g^{mk}_{\kappa m}-g^{m\kappa}_{\mu m}\bar{r}^{kl}_{\kappa\nu}-g^{m\kappa}_{\nu m}\bar{r}^{kl}_{\mu\kappa}+\bar{r}^{ml}_{\mu\nu}f^{k}_{m}+\bar{r}^{km}_{\mu\nu}f^{l}_{m}\}-\tfrac{1}{2}\,\bar{r}^{pq}_{ij}\{-2\hat{g}^{kl}_{pq}+2\bar{u}^{kl}_{pq}+\bar{r}^{k\kappa}_{pq}g^{ml}_{\kappa m}$$
$$+\bar{r}^{\kappa l}_{pq}g^{mk}_{\kappa m}-g^{m\kappa}_{pm}\bar{r}^{kl}_{\kappa q}-g^{m\kappa}_{qm}r^{kl}_{p\kappa}+\bar{r}^{ml}_{pq}f^{k}_{m}+\bar{r}^{km}_{pq}f^{l}_{m}\}$$
$$=-2(\mathscr{V}^{\dagger})^{kl}_{ij}+2\mathscr{U}^{kl}_{ij}+\mathscr{Q}^{kl}_{ij}+\tilde{\mathscr{Q}}^{kl}_{ij}+\mathscr{F}^{kl}_{ij}. \tag{E8}$$

For the definition of $(\mathscr{V}^{\dagger})^{kl}_{ij}$ see Eq. (D6c). We further need

$$\mathscr{U}^{kl}_{ij}=(\overline{r\bar{u}})^{kl}_{ij}-\tfrac{1}{2}\,\bar{r}^{pq}_{ij}\bar{u}^{kl}_{pq}=\tfrac{3}{2}\,\delta^{kl}_{ij}-\tfrac{1}{2}\,\bar{r}^{pq}_{ij}\bar{u}^{kl}_{pq}, \tag{E9}$$

$$\mathscr{Q}^{kl}_{ij}=\mathscr{X}^{k\kappa}_{ij}g^{ml}_{\kappa m}+\mathscr{X}^{\kappa l}_{ij}g^{mk}_{\kappa m}, \tag{E10}$$

$$\tilde{\mathscr{Q}}^{kl}_{ij}=\tfrac{1}{2}\,(-\bar{r}^{\mu\nu}_{ij}g^{m\kappa}_{\mu m}\bar{r}^{kl}_{\kappa\nu}-\bar{r}^{\mu\nu}_{ij}g^{m\kappa}_{\nu m}\bar{r}^{kl}_{\mu\kappa}+\bar{r}^{pq}_{ij}g^{m\kappa}_{pm}\bar{r}^{kl}_{\kappa p}$$
$$+\bar{r}^{pq}_{ij}g^{m\kappa}_{qm}\bar{r}^{kl}_{p\kappa}), \tag{E11}$$

$$\mathscr{F}^{kl}_{ij}=\mathscr{X}^{ml}_{ij}f^{k}_{m}+\mathscr{X}^{km}_{ij}f^{l}_{m}. \tag{E12}$$

All five expressions on the last r.h.s. of Eq. (E8) are differences between exact quantities and their approximation in the given basis. Equations (D6c), (E9), (E10), and (E12) are evaluated easily. Equations (E10) and (E11) result from the commutator of $\hat{K}$ with $\hat{r}_{12}$. The standard approximation A consists in neglecting Eqs. (E10), (E11), and (E12). It has been shown in the Appendix of Ref. 12 that the error due to neglect of Eq. (E10) goes as L^{-5}, that due to neglect of Eq. (E11) as L^{-7}. It is hence justified—in the standard approximation B—to neglect Eq. (E11) but to take care of Eq. (E10). Equation (E12) ought to be kept even in the standard approximation A. We shall comment on this at the end of this Appendix. It is perfectly in the spirit of the standard approximation (A or B) to replace the sum over κ in Eq. (E10) by a sum over r, i.e., to take

$$\mathscr{Q}^{kl}_{ij}\overset{\text{s.a.}}{=}\mathscr{X}^{kr}_{ij}g^{ml}_{rm}+\mathscr{X}^{rl}_{ij}g^{mk}_{rm} \tag{E13}$$

Of course, instead of from Eq. (E6a) one could as well have started from Eq. (E6b) with the result

$$\mathscr{B}^{kl}_{ij}=\tfrac{1}{2}\{-[\overline{f,r}]^{\mu\kappa}_{ij}+f^{\nu}_{i}\bar{r}^{\mu\kappa}_{\nu j}+f^{\nu}_{j}\bar{r}^{\mu\kappa}_{i\nu}\}\bar{r}^{kl}_{\mu\kappa}$$
$$-\tfrac{1}{2}\{-[\overline{f,r}]^{pr}_{ij}+f^{q}_{i}\bar{r}^{pr}_{qj}+f^{q}_{j}\bar{r}^{pr}_{iq}\}\bar{r}^{kl}_{pr},$$
$$=2\mathscr{V}^{kl}_{ij}-2\tilde{\mathscr{U}}^{kl}_{ij}+(\mathscr{Q}^{\dagger})^{kl}_{ij}+(\tilde{\mathscr{Q}}^{\dagger})^{kl}_{ij}+(\mathscr{F}^{\dagger})^{kl}_{ij}, \tag{E14}$$

$$\tilde{\mathscr{U}}^{kl}_{ij}=(\overline{ur})^{kl}_{ij}-\tfrac{1}{2}\bar{u}^{pq}_{ij}\bar{r}^{kl}_{pq}=\tfrac{1}{2}\delta^{kl}_{ij}-\tfrac{1}{2}\bar{u}^{pq}_{ij}\bar{r}^{kl}_{pq}. \tag{E15}$$

It is recommended to define [starting from Eq. (E9)]

$$(\mathscr{U}^{\dagger})^{kl}_{ij}=(\overline{\bar{u}^{\dagger}\bar{r}})^{kl}_{ij}-\tfrac{1}{2}(\bar{u}^{\dagger})^{pq}_{ij}\bar{r}^{kl}_{pq}=\tfrac{3}{2}\delta^{kl}_{ij}-\tfrac{1}{2}(\bar{u}^{\dagger})^{pq}_{ij}\bar{r}^{kl}_{pq}. \tag{E16}$$

Noting that u is neither Hermitean nor anti-Hermitean but that

$$(g-u)^{\dagger}=u-g;\quad u^{\dagger}=2g-u \tag{E17}$$

we can reformulate Eq. (E16) to

$$(\mathscr{U}^{\dagger})^{kl}_{ij}=2(\overline{gr})^{kl}_{ij}-(\overline{ur})^{kl}_{ij}-\bar{g}^{pq}_{ij}\bar{r}^{kl}_{pq}+\tfrac{1}{2}\bar{u}^{pq}_{ij}\bar{r}^{kl}_{pq} \tag{E18}$$

or Eq. (E15) to

$$\tilde{\mathscr{U}}^{kl}_{ij}=-(\mathscr{U}^{\dagger})^{kl}_{ij}+2\mathscr{V}^{kl}_{ij}. \tag{E19}$$

This allows the reformulation of Eq. (E14) to

$$\mathscr{B}^{kl}_{ij}=-2\mathscr{V}^{kl}_{ij}+2(\mathscr{U}^{\dagger})^{kl}_{ij}+(\mathscr{Q}^{\dagger})^{kl}_{ij}+(\tilde{\mathscr{Q}}^{\dagger})^{kl}_{ij}+(\mathscr{F}^{\dagger})^{kl}_{ij}. \tag{E20}$$

Neglecting $\tilde{\mathscr{Q}}$ and taking the average of Eqs. (E8) and (E20) we get

$$\mathscr{B}_{ij}^{kl} \overset{\text{s.a.}}{=} (-\mathscr{V}-\mathscr{V}^{\dagger}+\mathscr{U}+\mathscr{U}^{\dagger})_{ij}^{kl}+\tfrac{1}{2}(\mathscr{Q}+\mathscr{Q}^{\dagger}+\mathscr{F}+\mathscr{F}^{\dagger})_{ij}^{kl}. \tag{E21}$$

We can now renounce on the use of the extended Brillouin theorem, i.e., we go back to the original expansion (E1). What we have done in Eq. (E20) is to take the first term on the last r.h.s. of Eq. (E1) minus 1/2 of the second and third terms. What we still miss are the other halfs of the second and third terms as well as the entire last term, i.e.,

$$-\tfrac{1}{2}\bar{r}_{ij}^{pq}f_{q}^{\kappa}\bar{r}_{pk}^{kl}-\tfrac{1}{2}\bar{r}_{ij}^{p\nu}f_{\nu}^{r}\bar{r}_{pr}^{kl}+\bar{r}_{ij}^{pq}f_{q}^{r}\bar{r}_{pr}^{kl}. \tag{E22}$$

The first two terms in Eq. (E22) have already been taken care of, they must just be multiplied by a factor 2. Hence all expressions where we sum over p,q must be taken twice and the last term in Eq. (E22) must finally be added.

Numerical tests have indicated that one does not gain much in adding the correction term (E22), which confirms (fortunately) that the extended Brillouin theorem is a justified assumption.

Let us mention that even the ordinary Brillouin theorem need not be assumed to hold. This alternative has no advantage in the present case, but is useful in a multiconfigurational approach. The terms with f_{κ}^{k}, etc., in Eq. (E6) can then be written as

$$f_{\kappa}^{k}=h_{\kappa}^{k}+g_{m\kappa}^{mk}-g_{\kappa m}^{mk}. \tag{E23}$$

One sees that this leads to a cancellation of terms like $\bar{r}_{\mu\nu}^{\kappa l}g_{\kappa m}^{mk}$ in Eq. (E8) with the appearance of terms such qas $r_{\mu\nu}^{kl}g_{m\kappa}^{mk}$ instead. The final expressions are hardly more complicated.

The full expression involving $\mathscr{R}_0$, F_N, and $\mathscr{R}$ in Eq. (11e) is

$$\langle 0|\mathscr{R}_0^{\dagger}\tilde{a}_{kl}^{ij}(F_N\mathscr{R})_C|0\rangle = =\tfrac{1}{2}\mathscr{B}_{kl}^{mn}c_{mn}^{ij}-\tfrac{1}{2}\mathscr{X}_{kl}^{mn}(c_{mn}^{oj}f_{o}^{i}+c_{mn}^{io}f_{o}^{j}). \tag{E24}$$

Let us assume that the Fock operator is diagonalized, i.e., $f_{o}^{i}=\delta_{o}^{i}f_{i}^{i}$. Then the r.h.s. of Eq. (E24) can be rewritten as

$$\mathscr{B}_{kl}^{mn}(i,j)c_{mn}^{ij}, \tag{E25}$$

$$\begin{aligned}\mathscr{B}_{kl}^{mn}(i,j)&=\mathscr{B}_{kl}^{mn}-\mathscr{X}_{kl}^{mn}(f_{i}^{i}+f_{j}^{i})\\&=-(\mathscr{V}+\mathscr{V}^{\dagger}-\mathscr{U}^{\dagger}-\mathscr{U})_{kl}^{mn}-\tfrac{1}{2}(\mathscr{Q}+\mathscr{Q}^{\dagger})_{kl}^{mn}\\&\quad+\mathscr{X}_{kl}^{mn}(f_{m}^{m}+f_{n}^{n}-f_{i}^{i}-f_{j}^{i}).\end{aligned} \tag{E26}$$

In the case that one limits oneself to coefficients c_{ij}^{ij} the contributions involving the f_{m}^{m}, etc., cancel completely.

If one takes the meaning of the approximation A literally, one should only neglect the terms with $\mathscr{Q}$ in Eq. (E26) within this approximation, but keep those with f. In our previous calculations with approximation A (which means essentially in MP2-R12) we have also neglected the last expression on the last r.h.s. of Eq. (E26). The historical reason for this is that originally we only considered that $c_{kl}^{ij}=c_{ij}^{ij}=c_{ij}$ in Eq. (E25) is diagonal. In this case the last term in Eq. (E26) vanishes automatically. In the orbital invariant approach introduced later[16] allowing for $(ij)\neq(m,n)$, the f_{m}^{m}, etc., no longer cancel. Nevertheless inclusion of the last term in Eq. (E26) does not change very much, such that it remains justified to neglect them on MP2-R12 level.

APPENDIX F: TRIPLE CONTRACTIONS INVOLVING THE TWO ELECTRON INTERACTION

We need to evaluate the following contraction in the standard approximation (diagrammatic fragments d10.8 on Fig. 10)

$$\mathscr{Z}_{ij,p}^{kl,q}=\bar{R}_{ij}^{\alpha\beta}\bar{g}_{p\beta}^{q\gamma}\bar{R}_{\alpha\gamma}^{kl}. \tag{F1}$$

We decompose the antisymmetrized vertex $\bar{g}$ into its primitive components

d10.8a: $$X_{ij,p}^{kl,q}=\bar{R}_{ij}^{\alpha\beta}g_{p\beta}^{q\gamma}\bar{R}_{\alpha\gamma}^{kl}, \tag{F2a}$$

d10.8b: $$Y_{ij,p}^{kl,q}=\bar{R}_{ij}^{\alpha\beta}g_{\beta p}^{q\gamma}\bar{R}_{\alpha\gamma}^{kl} \tag{F2b}$$

because their l expansion is different. Although these contractions have, in principle, been treated in Ref. 12, we now present an improved strategy, due to Wim Klopper.[41] First we see that Eq. (F2a) means explicitly

$$X_{ij,p}^{kl,q}\overset{\text{s.a.}}{=}\bar{r}_{ij}^{\kappa\lambda}g_{p\kappa}^{q\mu}\bar{r}_{\mu\lambda}^{kl}-\bar{r}_{ij}^{rs}g_{pr}^{q\mu}\bar{r}_{\mu s}^{kl}-r_{ij}^{\kappa s}g_{p\kappa}^{qt}\bar{r}_{ts}^{kl}+\bar{r}_{ij}^{rs}g_{pr}^{qt}\bar{r}_{ts}^{kl} \tag{F3}$$

It was argued in Ref. 12 that

$$\bar{g}_{pr}^{q\mu}=0 \quad \text{for} \quad \mu\neq s \tag{F4}$$

which is somewhat analogous to the extended Brillouin condition[12] $f_{\nu}^{\mu}=0$ for $\mu=s$. In assuming that Eqs. (F4) holds, (F2a) reduces to

$$X_{ij,p}^{kl,q}\approx\bar{r}_{ij}^{\kappa\lambda}g_{p\kappa}^{q\mu}\bar{r}_{\mu\lambda}^{kl}-\bar{r}_{ij}^{rs}g_{pr}^{qt}\bar{r}_{ts}^{kl}. \tag{F5}$$

It is, however, not necessary to make assumption (F4). We rather use the fact that the one-electron operator

$$\hat{J}=g_{q\kappa}^{p\mu}a_{\mu}^{\kappa} \tag{F6}$$

is of Coulomb type—and hence local—and commutes with r_{12}. This allows us to rewrite

$$\begin{aligned}(rJ)_{ij,p}^{\mu\lambda,q}&=r_{ij}^{\kappa\lambda}g_{p\kappa}^{q\mu}+r_{ij}^{\mu\kappa}g_{p\kappa}^{q\lambda}\\&=g_{pi}^{q\kappa}r_{\kappa j}^{\mu\lambda}+g_{pj}^{q\kappa}r_{\kappa i}^{\lambda\mu}\\&=(Jr)_{ij,p}^{\mu\lambda,q},\end{aligned} \tag{F7a}$$

$$\begin{aligned}(Jr)_{\kappa\lambda,p}^{kl,q}&=g_{p\kappa}^{q\mu}r_{\mu\lambda}^{kl}+g_{p\lambda}^{q\mu}r_{\kappa\mu}^{kl}\\&=r_{\kappa\lambda}^{\mu l}g_{p\mu}^{qk}+r_{\kappa\lambda}^{k\mu}g_{p\mu}^{ql}\\&=(rJ)_{\kappa\lambda,p}^{kl,q}.\end{aligned} \tag{F7b}$$

We insert Eq. (F7a) into one half of Eqs. (F2a) and (F7b) into the other half. We define

$$\mathscr{Y}_{rs}^{ii}=\mathscr{X}_{rs}^{ij}-\tfrac{1}{2}(\bar{r}^{2})_{rs}^{ij}=\tfrac{1}{2}(\bar{r}^{2})_{rs}^{ij}-\tfrac{1}{2}\,\bar{r}_{rs}^{pq}\bar{r}_{pq}^{ij}. \tag{F8}$$

The result is then

$$X_{ij,p}^{kl,q}=g_{pi}^{q\kappa}\mathscr{Y}_{kj}^{kl}+g_{pj}^{q\kappa}\mathscr{Y}_{i\kappa}^{kl}+\mathscr{Y}_{ij}^{k\kappa}g_{p\kappa}^{ql}+\mathscr{Y}_{ij}^{\kappa l}g_{p\kappa}^{qk}+\bar{r}_{ij}^{rs}g_{pr}^{qt}\bar{r}_{ts}^{kl}. \tag{F9}$$

The summation over κ in Eq. (F9) can be replaced by a summation over t.

A trick like Eq. (F7) does not apply to Eq. (F2b) since $g^{p\mu}_{\kappa q}a^{\kappa}_{p}$ is an exchange-type operator which does not commute with r_{12}. We get explicitly

$$Y^{kl,q}_{ij,p}\overset{\text{s.a.}}{=}r^{\kappa\lambda}_{ij}g^{q\mu}_{\kappa p}r^{kl}_{\lambda\mu}-r^{rs}_{ij}g^{q\lambda}_{sp}r^{kl}_{\lambda r}-r^{\kappa t}_{ij}g^{qr}_{\kappa q}r^{kl}_{tr}+r^{rs}_{ij}g^{qt}_{sp}r^{kl}_{rt}. \tag{F10}$$

The first term in Eq. (F10) is expressible as a three-electron integral

$$\langle i(1)j(2)p(3)|r_{12}g_{13}r_{23}|q(1)k(2)l(3)\rangle. \tag{F11a}$$

The next two terms involve

$$\langle s(1)p(2)r(3)|g_{13}r_{23}|q(1)k(2)l(3)\rangle, \tag{F11b}$$

$$\langle i(1)j(2)p(3)|r_{12}g_{13}|q(1)t(2)r(3)\rangle. \tag{F11c}$$

A partial wave expansion of Eqs. (F11b) and (F11c) breaks off after a finite number of terms, that of Eq. (F11a) has partial wave increments that go as $(l+\frac{1}{2})^{-8}$. This means if the basis is saturated up to the critical L, any of the first three terms in Eq. (F10) are (except for spin) well presented by the last term. The error in neglecting Eq. (F10) altogether goes then with $(L+1)^{-7}$.

APPENDIX G: QUADRUPLE CONTRACTIONS

We have to consider the expressions corresponding to diagrams on Fig. 10(d)

$$\text{d10.9:}\quad \mathscr{P}^{kl}_{ij}=\tfrac{1}{4}\,\bar{R}^{\alpha\beta}_{ij}\bar{g}^{\gamma\delta}_{\alpha\beta}\bar{R}^{kl}_{\gamma\delta}, \tag{G1a}$$

$$\text{d10.10:}\quad \tfrac{1}{2}\,\bar{R}^{\alpha\beta}_{ij}\bar{g}^{\gamma\delta}_{nm}\bar{R}^{kl}_{\alpha\gamma}\bar{R}^{op}_{\beta\delta} \tag{G1b}$$

(here o and p count occupied spin–orbitals). In the standard approximation (G1a) becomes

$$\begin{aligned}\mathscr{P}^{kl}_{ij}&\overset{\text{s.a.}}{=}\tfrac{1}{4}\bar{r}^{\mu\nu}_{ij}\bar{g}^{\kappa\lambda}_{\mu\nu}\bar{r}^{kl}_{\kappa\lambda}-\tfrac{1}{4}\bar{r}^{\mu\nu}_{ij}\bar{g}^{pq}_{\mu\nu}\bar{r}^{kl}_{pq}-\tfrac{1}{4}\bar{r}^{rs}_{ij}\bar{g}^{\kappa\lambda}_{rs}\bar{r}^{kl}_{\kappa\lambda}+\tfrac{1}{4}\,\bar{r}^{rs}_{ij}\bar{g}^{pq}_{rs}\bar{r}^{rs}_{pq},\\ &=\bar{r}^{kl}_{ij}-\tfrac{1}{2}\,\delta^{pq}_{ij}\bar{r}^{kl}_{pq}-\tfrac{1}{2}\,\bar{r}^{rs}_{ij}\delta^{kl}_{rs}+\tfrac{1}{4}\,\bar{r}^{rs}_{ij}\bar{g}^{pq}_{rs}\bar{r}^{rs}_{pq},\\ &=\tfrac{1}{4}\,\bar{r}^{rs}_{ij}\bar{g}^{pq}_{rs}\bar{r}^{rs}_{pq}-\bar{r}^{kl}_{ij}.\end{aligned} \tag{G2}$$

From Eq. (G1b) we finally get terms like

$$\begin{aligned}R^{\kappa\lambda}_{ij}g^{\mu\nu}_{nm}R^{kl}_{\kappa\mu}R^{op}_{\lambda\nu}=&\,r^{\kappa\lambda}_{ij}g^{\mu\nu}_{nm}r^{kl}_{\kappa\mu}r^{op}_{\lambda\nu}-r^{pq}_{ij}g^{\mu\nu}_{nm}r^{kl}_{p\mu}r^{op}_{q\nu}\\ &-r^{p\lambda}_{ij}g^{r\nu}_{nm}r^{kl}_{pr}r^{op}_{\lambda\nu}-r^{\kappa q}_{ij}g^{\mu s}_{nm}r^{kl}_{\kappa\mu}r^{op}_{qs}\\ &+r^{pq}_{ij}g^{r\nu}_{nm}r^{kl}_{pr}r^{op}_{q\nu}+r^{pq}_{ij}g^{\mu s}_{nm}r^{kl}_{p\mu}r^{op}_{qs}.\end{aligned} \tag{G3}$$

The first term in the r.h.s. of Eq. (G3) is a four electron integral

$$\langle i(1)j(2)n(3)m(4)|r_{12}g_{34}r_{13}r_{24}|k(1)o(2)l(3)p(4)\rangle. \tag{G4a}$$

The second term involves

$$\langle n(1)m(2)p(3)q(4)|g_{12}r_{13}r_{24}|l(1)p(2)k(3)o(4)\rangle. \tag{G4b}$$

Similar expressions arise for the third and fourth terms, while the fifth term involves

$$\langle n(1)m(2)q(3)|g_{12}r_{23}|r(1)p(2)o(3)\rangle. \tag{G4c}$$

Again the sixth term is similar.

As shown in Appendix B, the partial wave increments of Eq. (G4a) decrease at least as $(l+\frac{1}{2})^{-12}$, those to Eqs. (G4a) and (G4b) break off after a finite number of terms.

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