The distinguishable cluster approach from a screened Coulomb formalism

Daniel Kats

Articles you may be interested in

A state-specific partially internally contracted multireference coupled cluster approach
J. Chem. Phys. **134**, 214116 (2011); 10.1063/1.3592494

An adaptive coupled-cluster theory: @CC approach
J. Chem. Phys. **133**, 244112 (2010); 10.1063/1.3515476

Local correlation calculations using standard and renormalized coupled-cluster approaches
J. Chem. Phys. **131**, 114109 (2009); 10.1063/1.3218842

An explicitly spin-free compact open-shell coupled cluster theory using a multireference combinatoric exponential ansatz: Formal development and pilot applications
J. Chem. Phys. **131**, 044124 (2009); 10.1063/1.3185356

Development of a linear response theory based on a state-specific multireference coupled cluster formalism
J. Chem. Phys. **112**, 7939 (2000); 10.1063/1.481395
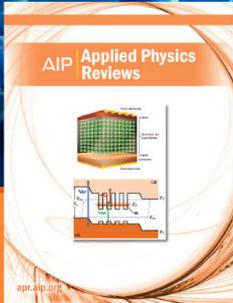
The distinguishable cluster approach from a screened Coulomb formalism

Daniel Kats

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

The distinguishable cluster doubles equations have been derived starting from an effective screened Coulomb formalism and a particle-hole symmetric formulation of the Fock matrix. A perturbative triples correction to the distinguishable cluster with singles and doubles (DCSD) has been introduced employing the screened integrals. It is shown that the resulting DCSD(T) method is more accurate than DCSD for reaction energies and is less sensitive to the static correlation than coupled cluster with singles and doubles with a perturbative triples correction. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4940398]

I. INTRODUCTION

One of the main advantages of the coupled-cluster theory[1] is the smooth convergence to full configuration interaction results by including higher excitation levels to the cluster operator. This property and the fact that already coupled cluster with singles and doubles (CCSD) with a perturbative triples correction (CCSD(T))[2] yields very accurate results has led to the dominance of the coupled-cluster theories (and their perturbative approximations) in wavefunction method applications.

The single-reference coupled-cluster theory is, however, much less suited for applications with a substantial multi-reference character. Recent advances in treating strong correlation with single-reference methods[3–11] have demonstrated that it is indeed a deficiency of the core coupled-cluster formalism. Besides, there are many methods which systematically produce more accurate results than CCSD even in the single reference regime.[12–17] This raises a question whether the coupled-cluster hierarchy is really the best possible way to approach the full configuration interaction limit, or there are other hierarchies which would converge faster and be less sensitive to the strong correlation.

One possible starting point for such an hierarchy is the distinguishable cluster (DC) approach.[17] It was derived as an *ad hoc* modification of the coupled-cluster doubles (CCD) amplitude equations and has shown very promising results in various single and multi-reference benchmark calculations.[17–19] However, if one naively adds the perturbative triples correction as in CCSD(T) to the DC with singles and doubles (DCSD) method, the energies become much too low, and also relative energies become worse (cf. Sec. III). In this publication, an alternative derivation of DCD equations is presented, which suggests a different formulation of the perturbative triples equations for DCSD(T).

The new derivation utilizes a modified electron-electron Coulomb repulsion. An effective interaction between two electrons is influenced by other electrons in the system, and a conventional way to account for this screening is by solving the amplitude equations. Here, we will present an alternative formulation which is related to the dressed coupled cluster formalism[20] (where the Hamilton operator is replaced by a singles similarity transformed Hamiltonian). In this case, the screening is incorporated in the two-electron operator.

Another important basis for the derivation is the particle-hole (p-h) symmetry of the equations. It is known for a long time (e.g., Ref. 21) that the second-quantization formalism is intrinsically particle-hole symmetric, i.e., replacing creation operators by annihilation operators and vice versa, and at the same time inverting occupation in the reference occupation vector does not change the resulting equations. Therefore, here we insist on this symmetry in our equations.

II. THEORY

A. Local particle-hole (lph) symmetry

As noted in the Introduction, the p-h symmetry of the equations is automatically satisfied for wavefunction based theories (if it is not destroyed explicitly by the underlying approximations). Although it does not mean that a p-h symmetric method is generally more accurate, it can be seen as an important characteristic of a wavefunction method. It is in some sense an analog of the invariance of a method with respect to orbital rotations within occupied or virtual subspaces, i.e., this invariance does not necessarily improve the results, but it is nevertheless a desired property, since the exact treatment does possess it.

One can introduce an even more restrictive symmetry to the equations by requiring that all loops in the diagrammatic representation have to be p-h symmetrical *individually*, i.e., for each loop in every diagram there has to exist a corresponding diagram with arrows going in the opposite direction. One can show that this kind of symmetry is related to the particle-number conservation.[22,23] We will call this symmetry *lph symmetry*.

The two-electron-integral contributions to the Fock matrix in the conventional formulation do not reproduce the lph symmetry, since the summation runs over occupied indices only,

$$f_{\mu\nu} = h_{\mu\nu} + 2(kk|\mu\nu) - (\mu k|k\nu), \tag{1}$$

with f, h, and $(xx|xx)$ denoting the Fock matrix, the one-electron part, and the two-electron integrals, respectively, and $\mu, \nu, \ldots, i, j, k, \ldots$, and $a, b, c, \ldots$ denote atomic-orbital (AO), occupied, and virtual indices. Here, and in the following, we assume the summation over repeated indices and utilize the spin-free formalism with orthonormal orbitals (but it can be applied as well to the spin-orbital formalism or generalized to non-orthogonal orbitals). For a formulation in the spin-orbital formalism, see Appendix A. However, this symmetry violation is formal, since one can easily rewrite Eq. (1) in a lph-symmetric form, using a symmetrized projector matrix,

$$P_{\mu\nu} = c_{\mu k}^* c_{\nu k} = \frac{1}{2}\left(c_{\mu k}^* c_{\nu k} + S_{\mu\nu}^{-1} - c_{\mu a}^* c_{\nu a}\right), \qquad (2)$$

with c and S denoting molecular orbital coefficients and AO overlap,

$$
\begin{aligned}
f_{\mu\nu} = & \; h_{\mu\nu} + (kk|\mu\nu) - \frac{1}{2}(\mu k|k\nu) \\
& - \left((aa|\mu\nu) - \frac{1}{2}(\mu a|a\nu)\right) \\
& + S_{\rho\sigma}^{-1}\left((\rho\sigma|\mu\nu) - \frac{1}{2}(\mu\sigma|\rho\nu)\right).
\end{aligned}
\qquad (3)
$$

Obviously, this can be formulated in any basis spanning the whole molecular-orbital space. We have chosen the AO basis to emphasize that the last two terms in Eq. (3) do not depend on the number of particles or holes in the system and are therefore lph symmetrical by themselves. This p-h-symmetric reformulation does not affect the Fock matrix itself, but is essential for the derivation of a p-h-symmetric theory based on the screened-integral formalism.

B. Effective electron repulsion

The screening of the electron repulsion in the many-electron systems can be effectively accounted in several ways.[24–29] We introduce the screening by modifying electron densities in the electron-repulsion integrals (ERIs) in the direct-random-phase-approximation (RPA)[30–32] (or direct-ring CCD[33]) manner,

$$\tilde{\rho}_{ai} = \rho_{ai} + \tilde{T}_{ab}^{ij}\rho_{jb}. \qquad (4)$$

We have used contravariant amplitudes $\tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ba}^{ij}$ in this expression in order to guarantee the proper fermionic symmetry of the parameters: in the spin-orbital basis these correspond to the proper permutationally symmetric amplitudes, cf. Appendix A. The direct RPA corresponds to an infinite summation of all direct ring Feynman diagrams, i.e., pure fluctuations in the Fermi vacuum,[34] and can be evaluated very efficiently using only doubles amplitudes.[33]

Writing the Coulomb integrals with the screened densities results in density-fitting separable effective ERIs,

$$
\begin{aligned}
(\widetilde{ai}|\widetilde{bj}) = & \; (ai|bj) + \tilde{T}_{ac}^{ik}(kc|bj) + (ai|kc)\tilde{T}_{cb}^{kj} \\
& + \tilde{T}_{ac}^{ik}(kc|ld)\tilde{T}_{db}^{lj} = \tilde{Y}_{ai}^P \tilde{Y}_{bj}^P,
\end{aligned}
\qquad (5)
$$

with

$$
\begin{aligned}
\tilde{Y}_{ai}^P &= d_{ai}^P + \tilde{T}_{ab}^{ij} d_{jb}^P, \\
d_{ai}^P &= (ai|Q)(Q|P)^{-1/2},
\end{aligned}
\qquad (6)
$$

and P, Q — fitting basis. The separability of effective integrals using resolution of the identity (RI) with the RI basis scaling linearly with the system size is closely related to the size-extensivity of the method. Indeed, if we increase the system size by some amount of electrons, and the effective interaction is not linearly separable, then the electrons would feel more than a linear amount of the system extension, which may result in a not size-extensive energy. The DF separability in Eq. (5) does not rely on the localizability of the orbitals (as in the CCD effective ERIs, cf. Appendix A) and, therefore, is of interest for strongly correlated systems.

First, we introduce this screening in the ERIs in the Fock matrix, where one has to utilize its lph-symmetric form, Eq. (3), since otherwise the resulting equations would lack the lph symmetry. After inserting the screened densities, Eq. (4), in the Fock matrix by dressing the corresponding ERIs with the doubles amplitudes, the effective Fock matrices become

$$
\begin{aligned}
\widetilde{f_{ac}} &= h_{ac} + (kk|ac) - \frac{1}{2}(\widetilde{ak}|kc) \\
& \quad - \left((dd|ac) - \frac{1}{2}(ad|dc)\right) \\
& \quad + S_{\rho\sigma}^{-1}\left((\rho\sigma|ac) - \frac{1}{2}(a\sigma|\rho c)\right) \\
&= f_{ac} - \frac{1}{2}\tilde{T}_{ad}^{kl}(ld|kc), \\
\widetilde{f_{ji}} &= f_{ji} + \frac{1}{2}\tilde{T}_{bd}^{il}(ld|jb).
\end{aligned}
\qquad (7)
$$

We start with the MP2 equations, which employ now the screened Coulomb interaction, Eq. (5), rather than the bare one. This results in slightly modified p-h-RPA amplitude equations. In order to improve the accuracy of the method, one has to account for the particle-particle, particle-hole, and hole-hole interactions. It can be done by adding one additional diagram to the amplitude equations, first diagram in Figure 1. However, this diagram and the second diagram in Figure 1 originate from a single diagram in the spin-orbital formalism; therefore, also in the spatial-orbital formalism, one should add both diagrams in order to retain the lph symmetry in both formulations. Adding these intra-cluster interactions, Figure 1, one obtains the DCD amplitude equations,[17,18] Figure 2. Note that the screening from Eq. (4) does not affect these intra-cluster interactions. Prior to the screening the intra-cluster diagrams in Figure 1 represent two-electron contributions to two-electron interactions, i.e., do not introduce new fluctuations (which otherwise could result in double counting when the screening is applied).

After accounting for orbital relaxation,[18] the resulting method becomes exact for two electrons, which is a quite remarkable fact, since during this derivation we have never explicitly required this property.

FIG. 1. lph-symmetric version of intra-cluster interaction diagrams in the spin-summed formalism.
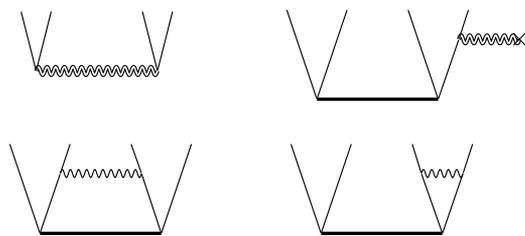
FIG. 2. lph-symmetric version of DCD diagrams using screened interactions (double lines) in the spin-summed formalism.

The same procedure can be used to obtain the CCD amplitude equations, but only in the spin-orbital formalism, cf. Appendix A.

C. Perturbative triples correction to DCSD

One way to improve upon DCSD is to use higher excitations. However, if one uses the same (T) equations as in CCSD(T) and simply replaces the CCSD amplitudes by the DCSD ones, the results deteriorate (cf. Sec. III). Instead of this naive approach, one can consistently use the screened Coulomb formalism to derive also the DCSD(T) equations. To this end, we have replaced the $(li|bj)$ and $(ac|bj)$ integrals in the standard (T) expressions by $(l\bar{i}|bj)$ and $(ac|\bar{b}j)$, respectively, and used the screened Fock matrices instead of the orbital energies in the denominator, cf. Appendix B. The resulting equations have to be solved iteratively, since the Fock matrices are no longer diagonal. However, in the usual (T) amplitude equations, only occupied-occupied and virtual-virtual blocks of the Fock matrices are present, and therefore it is possible to transform integrals and amplitudes to an effective pseudo-canonical basis, and solve the equations non-iteratively. Alternatively, one can work in the same framework as local correlation methods, where the Fock matrix is not diagonal as well (but still diagonal dominant), and solve the equations iteratively or use just the zeroth iteration (T0) instead.[35]

III. TEST CALCULATIONS

DCSD(T) equations from Sec. II C have been implemented into development version of MOLPRO[36,37] using local integrated tensor framework[38] and the iterative local perturbative algorithm from Ref. 39.

In all calculations, the aug-cc-pVTZ basis was used together with aug-cc-pVTZ/MP2FIT as the fitting basis set, and we made no local approximations in the pair or triple lists.

First, in order to test the accuracy of the DCSD(T) method, reaction energies for the test set from Ref. 16 have been calculated and compared to the back-corrected experimental values. The local domains for the virtual space (in projected atomic orbitals[40]) in the local DCSD(T) calculations were determined using the Boughton-Pulay procedure[41] (with threshold 0.985) and then extended to the neighbouring atoms (the iext = 1 option in MOLPRO). The local and basis-set incompleteness errors have been corrected by adding the $E_{DCSD-F12} - E_{DF-LDCSD}$ difference, where $E_{DCSD-F12}$ are

canonical DCSD-F12a energies[19] and $E_{DF-LDCSD}$ are local DCSD energies with the same local approximations as above. It has been shown in the previous studies[42] that even a much simpler correction using MP2 energies reduces these errors in reaction energies to few tens of kcal/mol, even if pair approximations are applied. Application of this type of correction to DF-LCCSD(T)[43] energies using the CCSD and DF-LCCSD energy differences results in the root-mean squared deviation of less than 0.1 kcal/mol compared to canonical CCSD(T)-F12a reaction energies. The density fitting error is negligible for relative energies[43] and is besides largely corrected by the above procedure. The root-mean squared, mean absolute, and maximal deviations in kcal/mol can be found in Table I. It is apparent from the results that the "naive" DCSD(T) approach does not provide any improvement over DCSD. At the same time, the DCSD(T) technique based on the screened integrals is clearly superior with respect to DCSD. This trend is also seen when comparing to estimated coupled cluster with singles, doubles, triples, and perturbative quadruples (CCSDT(Q)) results: the "naive" DCSD(T) reaction energies are worse than the DCSD results, and the screened (T) correction improves the DCSD results. The CCSDT(Q) complete-basis-set energies were estimated similarly to the high-accuracy extrapolated *ab initio* thermochemistry scheme[44] using the CCSD(T)-F12a energies[45,46] in the aug-cc-pVTZ basis ($E_{CCSD(T)-F12}^{aVTZ}$) by adding a full triples correction in the cc-pVTZ basis ($\Delta E_{T-(T)}^{VTZ} = E_{CCSDT}^{VTZ} - E_{CCSD(T)}^{VTZ}$) and a perturbative quadruples correction in the cc-pVDZ basis ($E_{(Q)}^{VDZ} = E_{CCSDT(Q)}^{VDZ} - E_{CCSDT}^{VDZ}$),

$$E_{CCSDT(Q)}^{CBS} \approx E_{CCSD(T)-F12}^{aVTZ} + \Delta E_{T-(T)}^{VTZ} + E_{(Q)}^{VDZ}. \quad (8)$$

For two reactions involving C_6H_6 and CH_3ONO molecules, we have used a simplified scheme with the $\Delta E_{T-(T)}^{VTZ} + E_{(Q)}^{VDZ}$ part replaced by $E_{CCSDT(Q)}^{VDZ} - E_{CCSDT(T)}^{VDZ}$ difference.

Absolute molecular energies are improved as well, as can be seen from Table II (the estimated CCSDT(Q) energies have been calculated using Eq. (8) or the simplified version of it for the C_6H_6 and CH_3ONO molecules). The variance of errors in DCSD(T) is almost three times smaller than in DCSD, which is important for relative energies, and also the mean error of DCSD is reduced after the screened (T) correction. The

TABLE I. Statistical analysis of the absolute deviations of CCSD(T)-F12a,[45,46] DCSD-F12a, naive DCSD(T)-F12a, and DCSD(T)-F12a reaction energies from experimental (top) and estimated CCSDT(Q)-F12a (bottom) ones (in kcal/mol).

	MAD	RMSD	MaxD
	Vs. experiment		
CCSD(T)-F12a	0.63	0.86	2.71
DCSD-F12a	0.91	1.16	2.96
DCSD(naiveT)-F12a	0.96	1.37	4.59
DCSD(T)-F12a	0.67	0.92	3.22
	Vs. CCSDT(Q)-F12a		
CCSD(T)-F12a	0.16	0.22	0.67
DCSD-F12a	0.80	1.15	3.78
DCSD(naiveT)-F12a	0.97	1.42	4.28
DCSD(T)-F12a	0.57	0.92	3.54

TABLE II. Signed mean deviation (MD), variance of deviations (S^2_{n-1}), and maximal deviation of CCSD(T)-F12a,[45,46] DCSD-F12a, naive DCSD(T)-F12a, and DCSD(T)-F12a molecular energies from estimated CCSDT(Q)-F12a ones (in mhartree).

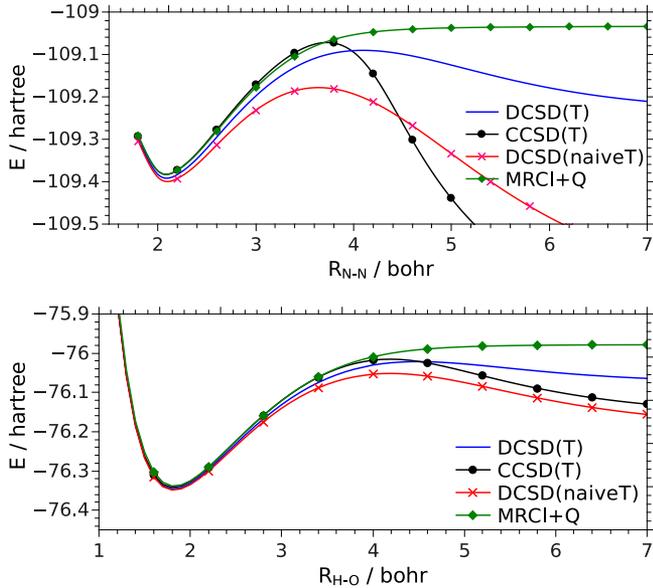|	MD	S^2_{n-1}	MaxD
CCSD(T)-F12a	1.5	7×10^{-4}	4.0
DCSD-F12a	9.7	3×10^{-2}	26.3
DCSD(naiveT)-F12a	−14.9	7×10^{-2}	31.3
DCSD(T)-F12a	−6.9	1×10^{-2}	13.6

FIG. 3. Potential energy curves. Top: N_2 dissociation. Bottom: symmetric double dissociation of H_2O with H–O–H angle fixed at 107.6°.

individual absolute and reaction energies can be found in the supplementary material.[47]

The sensitivity of DCSD(T) to the static correlation is tested by calculating dissociations of N_2 and H_2O using full domain local DCSD(T). The resulting potential energy curves are plotted in Figure 3. The DCSD(T) curves are more stable than CCSD(T) or DCSD(naiveT), i.e., the divergence starts at slightly larger distances and the curves are much more flat.

IV. CONCLUSIONS

Pure fluctuations in the Fermi vacuum can be efficiently summed up by using the direct RPA equations, with only doubles amplitudes.[33] However, taking additionally into account the particle and hole interactions results in higher excitations. In this publication, a separation of these two events is suggested, and a theory based on a screened effective Coulomb interaction is presented. It is shown that usage of direct RPA-like screening with antisymmetric amplitudes yields the DCD amplitude equations. Using these screened ERIs, a perturbative triples correction for DCSD is derived. The benchmarks of DCSD(T) for reaction and absolute molecular energies demonstrate that it is substantially more accurate than DCSD, as well as "naive" DCSD(T) (i.e., DCSD plus the standard (T) correction[2]), although the DCSD(T) results are still not as accurate as the CCSD(T) ones when

compared to the estimated CCSDT(Q) values. Furthermore, DCSD(T) is less sensitive to static correlation than CCSD(T) or a naive DCSD(T). The stability of DCSD(T) can be further improved by using completely renormalized triples[6] or by coupling triples and doubles equations[48] (DCSDT-1). This will be investigated in a forthcoming publication.

ACKNOWLEDGMENTS

APPENDIX A: SPIN-ORBITAL FORMULATION

In the spin-orbital formalism, the direct-RPA screening of the fluctuation density ρ_{AI} from Eq. (4) can be written as

$$\tilde{\rho}_{AI} = \rho_{AI} + T^{IJ}_{AB}\rho_{JB}, \tag{A1}$$

where capital letters denote spin-orbitals. The amplitudes T^{IJ}_{AB} should have the proper permutational fermionic symmetry which can be ensured by proper evaluation of the diagrams in the amplitude equations. Replacing the fluctuation density in the integrals by the dressed one results in the effective integrals and Fock matrices,

$$(\widetilde{AI}|\widetilde{BJ}) = (AI|BJ) + T^{IK}_{AC}(KC|BJ) + (AI|KC)T^{KJ}_{CB}$$
$$+ T^{IK}_{AC}(KC|LD)T^{LJ}_{DB}, \tag{A2}$$

$$\widetilde{f}_{AC} = h_{AC} + \frac{1}{2}\left((KK|AC) - (\widetilde{AK}|KC)\right)$$
$$- \frac{1}{2}((DD|AC) - (AD|DC))$$
$$+ \frac{1}{2}((RR|AC) - (AR|RC)) \tag{A3}$$
$$= f_{AC} - \frac{1}{2}T^{KL}_{AD}(LD|KC),$$

$$\widetilde{f}_{JI} = f_{JI} + \frac{1}{2}T^{IL}_{BD}(LD|JB),$$

with R denoting the general molecular orbital index. Inserting these effective quantities into the amplitude equation with the Fock and intra-cluster interactions, one again obtains the DCD amplitude equations, now in the spin-orbital formulation.

As noted in Sec. II B, in the spin-orbital formalism it is possible to use the same procedure to obtain the CCD amplitude equations. For this, additionally to the screening from Eq. (A2), one has to define the following dressed integrals:

$$(\widetilde{AC}|\widetilde{KI}) = \frac{1}{2}T^{IL}_{AD}(LC|KD),$$
$$(\widetilde{KI}|\widetilde{LJ}) = \frac{1}{4}T^{IJ}_{CD}(KC|LD), \tag{A4}$$
$$(\widetilde{AC}|\widetilde{BD}) = \frac{1}{4}T^{KL}_{AB}(KC|LD),$$

and these integrals should replace their undressed counterparts in the Fock matrix and in the amplitude equations. However, the form of the amplitude equations remains the same as in the DCD derivation.

APPENDIX B: DCSD(T) AMPLITUDE EQUATIONS

The DCSD amplitude equations[18,19] based on the CCSD factorization used in MOLPRO,[49]

$$
\begin{aligned}
R_{ab}^{ij} &= (ai|bj) + (ac|bd)D_{cd}^{ij} + \alpha_{ijkl}D_{ab}^{kl} - (kc|ld)T_{cd}^{ij}T_{ab}^{kl} \\
&\quad + \mathcal{P}(ia;jb)\Big\{ x_{ac}T_{cb}^{ij} - x_{ki}T_{ab}^{kj} + (ai|bc)t_c^j \\
&\quad - \big[(ac|kd)D_{cd}^{ij} + (ac|kj)t_c^i + k_{aikj}\big]t_b^k \\
&\quad + \tilde{T}_{ac}^{ik}Y_{cb}^{kj} - \tfrac{1}{2}T_{ac}^{ki}Z_{cb}^{kj} - T_{ac}^{kj}Z_{cb}^{ki}\Big\},
\end{aligned}
\tag{B1}
$$

$$
\begin{aligned}
r_a^i &= f_{ai} + \check{f}_{ac}t_c^i - \check{x}_{ki}t_a^k - [2(lc|ki) - (kc|li)]T_{ac}^{kl} \\
&\quad + [2(ai|kc) - (ki|ac)]t_c^k \\
&\quad + [f_{kc} + L_{cd}^{kl}t_d^l]\tilde{T}_{ca}^{ki} + (ac|kd)\tilde{D}_{cd}^{ik},
\end{aligned}
\tag{B2}
$$

with

$$
\begin{aligned}
\alpha_{ijkl} &= (ki|lj) + (kc|ld)D_{cd}^{ij} + t_c^i(kc|lj) + t_c^j(lc|ki), \\
x_{ac} &= \widetilde{f}_{ac} - [f_{kc} + L_{cd}^{kl}t_d^l]t_a^k + [2(ac|kd) - (kc|ad)]t_d^k, \\
x_{ki} &= \widetilde{f}_{ki} + f_{kc}t_c^i + t_c^l l_{lcki}, \\
\check{f}_{ac} &= \widetilde{f}_{ac} - \tfrac{1}{2}\tilde{T}_{ad}^{kl}(ld|kc), \\
\check{x}_{ki} &= x_{ki} + \tfrac{1}{2}\tilde{T}_{cd}^{il}(ld|kc), \\
Y_{cb}^{kj} &= (kc|bj) + (kc|bd)t_d^j - \tfrac{1}{2}\big[(kj|bc) + (bc|kd)t_d^j \\
&\quad - (kc|ld)\tilde{T}_{db}^{lj} + l_{kclj}t_b^l\big], \\
Z_{cb}^{kj} &= (kj|bc) + (bc|kd)t_d^j - k_{clkj}t_b^l, \\
k_{aikj} &= (ai|kj) + (ai|kc)t_c^j, \\
l_{lcki} &= 2(lc|ki) - (kc|li) + L_{dc}^{kl}t_d^i, \\
L_{cd}^{kl} &= 2(kc|ld) - (kd|lc), \\
D_{ab}^{ij} &= T_{ab}^{ij} + t_a^i t_b^j, \\
\tilde{T}_{ab}^{ij} &= 2T_{ab}^{ij} - T_{ab}^{ij}, \\
\mathcal{P}(ia;jb)X_{ab}^{ij} &= X_{ab}^{ij} + X_{ba}^{ji}.
\end{aligned}
\tag{B3}
$$

The screened (T) equations,

$$
R_{abc}^{ijk} = W_{abc}^{ijk} + \mathcal{P}(ia;jb,kc)\Big\{\widetilde{f}_{ad}T_{dbc}^{ijk} - \widetilde{f}_{li}T_{abc}^{ljk}\Big\},
\tag{B4}
$$

with

$$
\begin{aligned}
W_{abc}^{ijk} &= \mathcal{P}(ia;jb,kc)\,\mathcal{P}(jb;kc) \\
&\quad \times \Big\{(bd|\widetilde{ai})T_{dc}^{jk} - (lj|\widetilde{ai})T_{bc}^{lk}\Big\}, \\
\mathcal{P}(ia;jb,kc)X_{abc}^{ijk} &= X_{abc}^{ijk} + X_{bac}^{jik} + X_{cba}^{kji}.
\end{aligned}
\tag{B5}
$$

[1] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).
[2] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[3] J. Paldus, J. Čížek, and M. Takahashi, Phys. Rev. A **30**, 2193 (1984).
[4] P. Piecuch and J. Paldus, Int. J. Quantum Chem. **40**, 9 (1991).
[5] P. Piecuch, R. Tobola, and J. Paldus, Phys. Rev. A **54**, 1210 (1996).
[6] K. Kowalski and P. Piecuch, J. Chem. Phys. **113**, 18 (2000).
[7] J. B. Robinson and P. J. Knowles, J. Chem. Phys. **135**, 044113 (2011).
[8] D. W. Small and M. Head-Gordon, J. Chem. Phys. **137**, 114103 (2012).
[9] T. Stein, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **140**, 214113 (2014).
[10] K. Boguslawski, P. Tecmer, P. A. Limacher, P. A. Johnson, P. W. Ayers, P. Bultinck, S. D. Baerdemacker, and D. V. Neck, J. Chem. Phys. **140**, 214114 (2014).
[11] I. W. Bulik, T. M. Henderson, and G. E. Scuseria, J. Chem. Theory Comput. **11**, 3171 (2015).
[12] W. Meyer, Int. J. Quantum Chem., Symp. **5**, 341 (1971).
[13] M. Nooijen and R. J. Le Roy, J. Mol. Struct. **768**, 25 (2006).
[14] F. Neese, F. Wennmohs, and A. Hansen, J. Chem. Phys. **130**, 114108 (2009).
[15] L. M. J. Huntington and M. Nooijen, J. Chem. Phys. **133**, 184109 (2010).
[16] L. M. J. Huntington, A. Hansen, F. Neese, and M. Nooijen, J. Chem. Phys. **136**, 064101 (2012).
[17] D. Kats and F. R. Manby, J. Chem. Phys. **139**, 021102 (2013).
[18] D. Kats, J. Chem. Phys. **141**, 061101 (2014).
[19] D. Kats, D. Kreplin, H.-J. Werner, and F. R. Manby, J. Chem. Phys. **142**, 064111 (2015).
[20] H. Koch, A. S. de Merás, T. Helgaker, and O. Christiansen, J. Chem. Phys. **104**, 4157 (1996).
[21] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, 1981).
[22] D. Kats and D. Usvyat, "On the importance of the local particle–hole symmetry" (unpublished).
[23] O. Masur, D. Usvyat, and M. Schütz, J. Chem. Phys. **139**, 164116 (2013).
[24] L. Hedin, Phys. Rev. **139**, 796 (1965).
[25] F. Bechstedt, K. Tenelsen, B. Adolph, and R. Del Sole, Phys. Rev. Lett. **78**, 1528 (1997).
[26] S. Hirata and R. J. Bartlett, J. Chem. Phys. **112**, 7339 (2000).
[27] T. Miyake and F. Aryasetiawan, Phys. Rev. B **77**, 085122 (2008).
[28] J. J. Shepherd and A. Grüneis, Phys. Rev. Lett. **110**, 226401 (2013).
[29] M. Goldey, A. Dutoi, and M. Head-Gordon, Phys. Chem. Chem. Phys. **15**, 15869 (2013).
[30] D. Langreth and J. Perdew, Solid State Commun. **17**, 1425 (1975).
[31] J. Oddershede, *Adv. Quantum Chem.* (Elsevier, 1979), Vol. 11, p. 275.
[32] F. Furche, J. Chem. Phys. **129**, 114105 (2008).
[33] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys. **129**, 231101 (2008).
[34] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (Dover Publications, 1992).
[35] M. Schütz, J. Chem. Phys. **113**, 9986 (2000).
[36] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 242 (2012).
[37] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2015.1, a package of *ab initio* programs, 2015, see http://www.molpro.net.
[38] D. Kats and F. R. Manby, J. Chem. Phys. **138**, 144101 (2013).
[39] D. Kats, J. Chem. Phys. **141**, 244101 (2014).
[40] P. Pulay, Chem. Phys. Lett. **100**, 151 (1983).
[41] J. W. Boughton and P. Pulay, J. Comput. Chem. **14**, 736 (1993).
[42] J. Yang, G. K. L. Chan, F. R. Manby, M. Schütz, and H.-J. Werner, J. Chem. Phys. **136**, 144105 (2012).
[43] H.-J. Werner and M. Schütz, J. Chem. Phys. **135**, 144116 (2011).
[44] M. E. Harding, J. Vazquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, J. Chem. Phys. **128**, 114111 (2008).
[45] T. B. Adler, G. Knizia, and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[46] G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130**, 054104 (2009).
[47] See supplementary material at http://dx.doi.org/10.1063/1.4940398 for the molecular and reaction energies. For information on supplementary material, see http://www.aip.org/pubservs/epaps.html.
[48] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[49] C. Hampel, K. A. Peterson, and H.-J. Werner, Chem. Phys. Lett. **190**, 1 (1992).