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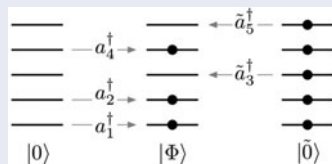# Particle–hole symmetry in many-body theories of electron correlation

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aInstitut für Theoretische Chemie, Universität Stuttgart, Stuttgart, Germany; bMax Planck Institute for Solid State Research, Stuttgart, Germany; cInstitut für Chemie, Humboldt-Universität zu Berlin, Berlin, Germany; dCentre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol, UK

ABSTRACT

Second-quantised creation and annihilation operators for fermionic particles anticommute, but the same is true for the creation and annihilation operators for holes. This introduces a symmetry into the quantum theory of fermions that is absent for bosons. In *ab initio* electronic structure theory, it is common to classify methods by the number of electrons for which the method returns exact results: for example Hartree–Fock theory is exact for one-electron systems, whereas coupled-cluster theory with single and double excitations is exact for two-electron systems. Here, we discuss the generalisation: methods based on approximate wavefunctions that are exact for *n*-particle systems are also exact for *n*-hole systems. Novel electron correlation methods that attempt to improve on the coupled-cluster framework sometimes retain this property, and sometimes lose it. Here, we argue for retaining particle–hole symmetry as a desirable design criterion of approximate electron correlation methods. Dispensing with it might lead to loss of *n*-representability of density matrices, and this in turn can lead to spurious long-range behaviour in the correlation energy.

1. Introduction

Since the widespread adoption of coupled-cluster (CC) theory in quantum chemistry [1–3], there have been many attempts to fix its deficiencies by including additional terms, or by leaving certain terms out. The former is perhaps best illustrated by the perturbative (T) correction [4], but also includes attempts to capture low-scaling contributions from variational CC theory [5]. Theories that resemble CC theory with single and double excitations (CCSD) but lack certain terms are more plentiful, and include linearised CC [1,6,7], various coupled electron-pair approximations [8], the *n*CC hierarchy from the Bartlett group [9], the pCCSD family of methods from the Nooijen group [10,11], the approximate coupled-pair approaches of Paldus *et al.* [12–14] and many others. Most recently, this class of methods has been joined by the distinguishable cluster approximation [15].

Deletion of terms from CCSD seems in many cases to improve accuracy, rather than reduce it. Many studies demonstrate that the approximate coupled-pair approach with approximate quadruples (ACPQ) is superior to the full CCSD method for strongly correlated systems [12–14,16]. At the same time, the accuracy of ACPQ in the weakly correlated regime is similar to that of CCSD [9,14]. On the other hand, the parameterised CCSD methods (pCCSD), developed as orbital-invariant extensions of CEPA methods, are much more accurate than CCSD for dynamical correlation (particularly the pCCSD(−1, 1) version), but like CCSD, they are completely unreliable for static correlation [10,11]. The pCCSD(1, 0) method is closely related to ACPQ (and equal to 2CC [9]) and can be used for strongly correlated systems, albeit at the expense of reduced accuracy for weakly correlated systems [10].

The distinguishable cluster doubles approach combines the strengths of the two approaches providing similar (or even higher) accuracy than ACPQ in the strongly correlated regime, and similar accuracy to pCCSD(−1, 1) in the weakly correlated regime [15,17,18]. Orbital relaxation in the distinguishable cluster method can be

handled in any of the standard ways for CC theory, i.e. using Brueckner orbitals, orbital optimisation or single excitations (distinguishabe cluster with singles and doubles - DCSD) [17].

It is widely recognised that in selecting subsets of diagrams to include in approximate correlation theories, certain design principles should be applied. For example, in most successful theories, full diagrammatic expressions are retained, which provides invariance to unitary transformations within the occupied orbitals, or within the virtuals, and extensivity in the ground-state energy. It is also reassuring to ensure exactness for two-electron systems and thereby, via extensivity, for an arbitrary number of non-interacting two-electron systems. The CCSD, pCCSD, ACP and DCSD methods all satisfy these three properties of orbital invariance, extensivity and exactness for two-electron systems.

Perhapsthere is another exactness property that can guide the construction of approximations, and can help to account for the surprising accuracy of DCSD. Here, we will argue that this additional criterion might be particle–hole symmetry.

Wigner's theorem identifies symmetry operations as either being unitary or anti-unitary, respectively satisfying

$$\langle \hat{U}\psi | \hat{U}\psi' \rangle = \langle \psi | \psi' \rangle$$
$$\langle \hat{A}\psi | \hat{A}\psi' \rangle = \langle \psi' | \psi \rangle,$$

which either commute or anti-commute with the Hamiltonian. The particle–hole operator $\hat{P}$ interchanges particles and holes, and for some Hamiltonians, such as the Bogoliubov-de Gennes Hamiltonian, $\hat{P}$ is an anti-commuting anti-unitary symmetry.

Here, however, we mean particle–hole symmetry in a different sense: we refer to the natural way in which the roles of particles and holes can be interchanged in fermionic calculations expressed in the language of second quantisation. Particle–hole symmetry in this sense was identified by Dirac, who describes [19, p. 252]

> a development of the theory of fermions that has no analogue for bosons. For fermions there are only the two alternatives of a state being occupied or unoccupied and *there is a symmetry between these two alternatives.* [Dirac's emphasis]

The creation and annihilation operators for holes are the Hermitian conjugates of the corresponding operators for particles:

$$\hat{\tilde{a}}_p = \hat{a}_p^\dagger \qquad \hat{\tilde{a}}_p^\dagger = \hat{a}_p$$

(here, we use tilde to denote quantities related to holes). The adjoint operation preserves the fermionic anti-commutation relation

$$[\hat{\tilde{a}}_p, \hat{\tilde{a}}_q^\dagger]_+ = [\hat{a}_p^\dagger, \hat{a}_q]_+ = \delta_{pq} ,$$

so the holes are fermions in just the same sense as the particles. Moreover, for a single site, the hole number operator $\hat{\tilde{n}} = \hat{\tilde{a}}^\dagger \hat{\tilde{a}}$ has the expected relation to the particle number operator: $\hat{\tilde{n}} = 1 - \hat{n}$.

There is no particular reason to prefer one representation over the other: proper fermionic states can be constructed by applying a string of particle creation operators to the zero particle-vacuum state

$$|\Phi\rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots |0\rangle,$$

or equally well by applying hole creation operators to the hole-vacuum state

$$|\Phi\rangle = \hat{\tilde{a}}_a^\dagger \hat{\tilde{a}}_b^\dagger \cdots |\tilde{0}\rangle.$$

Here, the hole vacuum $|\tilde{0}\rangle$ is the fully occupied state with one electron in each spin orbital, and a typical situation is illustrated in Figure 1.[1]

As we will show, this basic structure that is built into the quantum mechanics for fermions translates into a symmetry between particles and holes in approximate theories for the many-body problem derived from wavefunctions.

2. Theory

2.1. Particle–hole symmetry in electronic structure theory

Hartree–Fock (HF) theory is an exact theory for one-particle systems: both the HF and the exact wavefunction have the structure $\hat{a}_1^\dagger |0\rangle$ for some suitably constructed $\hat{a}_1^\dagger$. Similarly, HF is exact for single-hole systems, i.e. for $n - 1$ electrons in n spin-orbitals, because both the HF and exact wavefunctions have the form $\hat{\tilde{a}}_n^\dagger |\tilde{0}\rangle$. HF
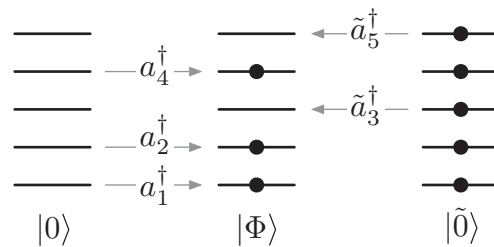

Figure 1. Construction of a particular state $|\Phi\rangle$ by creating particles in the vacuum ($\hat{a}_4^\dagger \hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle$), or equivalently by creating holes in the hole-vacuum ($\hat{\tilde{a}}_5^\dagger \hat{\tilde{a}}_3^\dagger |\tilde{0}\rangle$).

theory is extensive (setting aside for the moment the size-consistency limitations of the spin-restricted formulation) so it is exact for an arbitrary number of isolated one-particle or one-hole systems, or indeed for a mixture of the two. To give a concrete example, a HF calculation on fluorine (nine electrons) in the STO-3G basis set (5 spatial orbitals, so 10 spin orbitals) is exactly equivalent to full configuration interaction (full CI) in the same basis.

Correlated post-HF methods are often expressed in terms of excited determinants obtained from the HF ground-state determinant through the application of an excitation operator; for example, a singly excited determinant can be constructed as $|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i |\Phi\rangle$. It is clearly the case that each particle excitation operator is equivalent to a corresponding hole de-excitation operator, as in $\hat{a}_a^\dagger \hat{a}_i \equiv \hat{\tilde{a}}_a \hat{\tilde{a}}_i^\dagger$, so that each excited determinant can be constructed either by exciting particles or de-exciting holes. For this reason, a truncated CI expansion such as CI with single and double excitations (CISD), which is exact for systems of two particles, is simultaneously exact for systems of two holes; and analogous equivalences exist for all truncated CI methods.

Møller-Plesset perturbation theory of second order (MP2) is exact neither for systems of two particles nor two holes. It is normally thought of as a particle-pair theory – in the sense that the correlation energy is expressed as a sum of independent contributions for each electron pair – but it can just as well be viewed as a hole-pair theory, as seen by a simple reordering of summations.

CCSD is exact for two-electron systems and, through the extensivity of the method, for an arbitrary number of isolated two-electron systems. Because each diagram in the CCSD equations is accompanied by the diagram with particle and hole lines interchanged – and this feature is discussed in detail in what follows – it is also exact for two-hole systems. Again, extensivity provides that it is exact for any number of non-interacting two-hole systems, and indeed for any system composed of non-interacting fragments that each have either two particles or two holes.

Thus, all of the key wavefunction-based methods in quantum chemistry share the property that exactness for some particular model problem defined in terms of particles is reflected in exactness for the analogous model problem in which the role of particles and holes is interchanged.

This is typically not the case for methods that are not derived by substituting a wavefunction ansatz into the Schrödinger equation. For example, in the independent electron pair approximation (IEPA), the correlation energies from separate CI calculations on each electron pair are summed together to give an estimate of the total correlation energy – there is no IEPA wavefunction. The method is obviously exact if there is only a single pair of electrons (or any number of non-interacting pairs), but is not generally exact for systems with a single pair of holes.

2.2. Local particle–hole symmetry in wavefunction methods

As we have seen, the formulation of approximate wavefunctions in terms of second-quantised operators leads to a symmetry in the exactness properties of the resulting method. However, derivation of methods in this way leads to an even more restrictive particle-hole (PH) symmetry, the *local* PH (LPH) symmetry [20], which can be defined in terms of Goldstone diagrams. A method has LPH symmetry if the interchange of particle and hole in any loop of any diagram in the theory leads to another diagram in the theory (with the same factor). In the following, we will demonstrate that LPH symmetry emerges naturally when a theory is formulated in terms of a properly anti-symmetric state, and can therefore be viewed as an n-representability requirement for approximate theories.

A convenient way to discuss local particle–hole symmetry in second quantisation is by defining all operators in terms of one-electron excitation operators $\hat{\tau}_q^p = \hat{a}_p^\dagger \hat{a}_q$. Many-electron excited determinants can be written as products of these operators acting on the reference determinant

$$\left| \Phi_{ab\ldots}^{ij\ldots} \right\rangle = \hat{\tau}_i^a \hat{\tau}_j^b \cdots |\Phi\rangle \,,$$

and de-excitation operators correspond to the Hermitian conjugate:

$$\hat{\tau}_i^{a\dagger} = \hat{\tau}_a^i. \tag{1}$$

The two-electron part of the Hamiltonian can be written as $\frac{1}{2} \sum_{pqrs} (pq|rs) [\hat{\tau}_q^p \hat{\tau}_s^r - \delta_{qr} \hat{\tau}_s^p]$, and contractions of the operators can be realised using the well-known commutator relation,

$$\left[\hat{\tau}_q^p, \hat{\tau}_s^r \right] = \delta_{qr} \hat{\tau}_s^p - \delta_{ps} \hat{\tau}_q^r. \tag{2}$$

The two terms on the right-hand-side of Equation (2) show the origin of the LPH symmetry: if two one-electron operators are contracted together, two terms arise – one from the contraction of the inner creation and annihilation operators (which usually correspond to virtual orbitals), and one from the outer operators (usually corresponding to the occupied orbitals). Therefore, an expression coming from a wavefunction-based formalism can violate the LPH symmetry only if either the excitation operators in the Hamiltonian operator do not run over

the complete orbital space, or if the excitation operators in the wavefunction do not correspond to excitations from the occupied to the virtual space, but rather, for example, from the occupied to the occupied space. In the former case, the resulting Hamiltonian can lead to a violation of particle-number conservation, as discussed in Section 2.3. For example, if we restrict the excitation operator in the Fock operator to act only on occupied space, the corresponding correlated density matrix would have a non-zero trace. In the latter case, the resulting correlated wavefunction becomes contaminated by the reference determinant, since the correlated wavefunction is no longer orthogonal to the reference:

$$\langle\Phi|\sum_{ij} t_j^i \hat{\tau}_i^j |\Phi\rangle = \sum_i t_i^i.$$

Thus, if a theory can be formulated using second quantisation with number-conserving excitation operators, the resulting equations necessarily possess the LPH symmetry.

2.3. Local particle–hole symmetry and particle-number conservation

In this section, we will examine how the absence of PH or LPH symmetry affects one- and two-electron density matrices. For the sake of clarity, we restrict ourselves to the coupled-cluster doubles (CCD) theory and its approximations, but these results can be straightforwardly generalised.

2.3.1. Density matrices in diagrammatic approximations

The energy and amplitude equations in standard CC theory can be obtained by bra-projecting the electronic Schrödinger equation $\hat{H}|CC\rangle = E|CC\rangle$ with an exponentially parametrised wavefunction $|CC\rangle = \exp(\hat{T})|\Phi\rangle$ using the reference $\langle\Phi|$ or excited determinants $\langle\Phi|\hat{\tau}_\mu^\dagger$, respectively. Here, $\hat{H}$ is a normal-ordered Hamiltonian, which can conveniently be partitioned into the effective one-electron Fock operator $\hat{F}$ and the two-electron fluctuation potential $\hat{W}$. In the CCD theory, the cluster operator $\hat{T}$ is restricted to double excitations only:

$$\hat{T}_2 = \frac{1}{4}\sum_{ijab} T_{ab}^{ij}\hat{\tau}_{ij}^{ab}, \tag{3}$$

where T_{ab}^{ij} are the excitation amplitudes and $\hat{\tau}_{ij}^{ab} = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$ the excitation operators.

The diagrams entering the CCD amplitude equation

$$0 = R_{ij}^{ab} \equiv \left\langle\Phi\left|\hat{\tau}_{ij}^{ab\dagger}\left(\hat{W} + \hat{F}\hat{T}_2 + \hat{W}\hat{T}_2 + \tfrac{1}{2}\hat{W}\hat{T}_2^2\right)_C\right|\Phi\right\rangle, \tag{4}$$

where the subscript 'C' stands for 'connected', are PH symmetric. Moreover, as indicated in Section 2.2, they have LPH symmetry. This means that exchanging the roles of particle and hole in any loop of any diagram in R_{ij}^{ab} produces another diagram (with the correct factor) that also appears in R_{ij}^{ab}.

Approximate models, however, do not necessarily have this feature. Many approximate models have been devised by modifying the amplitude equation by direct removal, addition or rescaling of certain diagrams [8–10,12–15,21]. For ease of reference, we will denote such a modification of the residual expression as $\mathbb{M}R_{ij}^{ab}$. Such manipulations could lead to a loss of the LPH symmetry, as the latter is not commonly considered an essential constraint. As we demonstrate in what follows, violation of this symmetry can compromise particle-number conservation in density matrices.

In non-variational wavefunction-based theories such as projected CC, there are two distinct ways to define density matrices: (i) via derivatives of the energy Lagrangian [22] or (ii) directly using the wavefunction. The latter approach is very rare even within the CC model itself [23], and in approximate theories that lack an explicit form for the wavefunction, the energy derivative remains the only option.

Without an external perturbation, the CCD energy Lagrangian reads:

$$L\left(\overline{\mathbf{T}}, \mathbf{T}\right) = \left\langle\Phi\left|\left(\hat{W}\hat{T}_2\right)_C\right|\Phi\right\rangle + \overline{\mathbf{T}}\cdot\mathbf{R}, \tag{5}$$

where $\overline{\mathbf{T}}$ and $\mathbf{R}$ are the Lagrange-multiplier and residual vectors, respectively. If one adds external one-electron $\epsilon_1\hat{X}_1$ and two-electron $\epsilon_2\hat{X}_2$ perturbations with strengths ϵ_1 and ϵ_2, the CCD Lagrangian takes the form:

$$L\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right) = \left\langle\Phi\left|\left(\hat{W}\hat{T}_2 + \epsilon_2\hat{X}_2\hat{T}_2\right)_C\right|\Phi\right\rangle + \overline{\mathbf{T}}\cdot\left(\mathbf{R} + \mathbf{R}^X\right), \tag{6}$$

with

$$\left(R^X\right)_{ij}^{ab} = \left\langle\Phi\left|\hat{\tau}_{ij}^{ab\dagger}\left(\epsilon_2\hat{X}_2 + \epsilon_1\hat{X}_1\hat{T}_2 + \epsilon_2\hat{X}_2\hat{T}_2 + \tfrac{1}{2}\epsilon_2\hat{X}_2\hat{T}_2^2\right)_C\right|\Phi\right\rangle. \tag{7}$$

A physical property corresponding to the perturbation $\epsilon_1\hat{X}_1$ or $\epsilon_2\hat{X}_2$ can be evaluated as the derivative of the Lagrangian in Equation (6) with respect to ϵ_1 or ϵ_2, taken at zero perturbation strength:

$$\frac{dL\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right)}{d\epsilon_1}\Bigg|_{\epsilon_1=0} = \sum_{ijab} \overline{T}_{ab}^{ij} \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\dagger} \left(\hat{X}_1 \hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle$$

$$\equiv \sum_{pq} {}^1 D_{pq} X_{pq}, \qquad (8)$$

$$\frac{dL\left(\overline{\mathbf{T}}, \mathbf{T}; \epsilon_1, \epsilon_2\right)}{d\epsilon_2}\Bigg|_{\epsilon_2=0}$$

$$= \left\langle \Phi \left| \left(\hat{X}_2 \hat{T}_2\right)_{\mathrm{C}} \right| \Phi \right\rangle$$

$$+ \sum_{ijab} \overline{T}_{ab}^{ij} \left\langle \Phi \left| \hat{\tau}_{ij}^{ab\dagger} \left(\hat{X}_2 \left[1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2\right]\right)_{\mathrm{C}} \right| \Phi \right\rangle$$

$$\equiv \sum_{pqrs} {}^2 D_{pq,rs} X_{pq,rs}. \qquad (9)$$

Here, X_{pq} and $X_{pq,rs}$ are the integrals of the one-electron and two-electron perturbation operators, respectively. The expressions in Equations (8) and (9) serve as the definitions of the density matrices ${}^1 D_{pq}$ and ${}^2 D_{pq,rs}$. The correlation energy is expressed via these density matrices as

$$E_{\mathrm{corr}} = \sum_{pq} {}^1 D_{pq} F_{pq} + \sum_{pqrs} {}^2 D_{pq,rs} \left(pq|rs\right), \qquad (10)$$

where $(pq|rs)$ is an electron repulsion integral for spin-orbitals in the chemical notation.

In CCD, the diagrams stemming from the matrix elements in Equations (8) and (9) are LPH symmetric. In an approximate theory based on modified amplitude equations $\mathbb{M}\mathbf{R}$, this might no longer be the case, as this modification entails an identical modification $\mathbb{M}\mathbf{R}^X$ of the diagrams in the external perturbation part $\mathbf{R}^X$. Indeed, in case of explicit inclusion of a finite perturbation, it will appear either in the one-electron part of the Hamiltonian $\hat{F} \leftarrow \hat{F} + \hat{X}_1$ or the two-electron part $\hat{W} \leftarrow \hat{W} + \hat{X}_2$. Therefore, if $\mathbb{M}$ destroys the LPH or PH symmetry in the residual equations, the density matrix will lack it as well.

2.3.2. Particle–hole symmetry and the one-electron density matrix

We start by analysing the role of particle–hole symmetry in the one-electron density matrix of CCD, which has diagonal occupied and virtual blocks with the form

$$^1 D_{ij} = -\sum_{abk} \overline{T}_{ab}^{kj} T_{ab}^{ki},$$

$$^1 D_{ab} = \sum_{ijc} \overline{T}_{ac}^{ij} T_{bc}^{ij}. \qquad (11)$$

Since orbital relaxation is not included in the Lagrangian of Equation (6), the occupied-virtual blocks of the density matrix are zero. The definition in Equation (11) explicitly demonstrates the PH symmetry of the CCD density matrix: the trace of a post-HF density matrix should be zero, and this is obviously fulfilled here because $\Sigma_i {}^1 D_{ii} = -\Sigma_a {}^1 D_{aa}$.

Now, consider an approximate theory, where $\mathbb{M}$ affects the Fock-terms $\hat{F}\hat{T}$ of the CCD residual; in particular, we are interested in a modification $\mathbb{M}$ that breaks particle–hole symmetry. Such a modification might be one that selectively erases either the hole *or* the particle Fock contractions in the residual, but not both:

$$\mathbb{M}^{1-\mathrm{p}} R_{ij}^{ab} = \cdots - 0 \times \left[\sum_k T_{ab}^{ik} F_{kj} + T_{ab}^{kj} F_{ki}\right]$$

$$+ \left[\sum_c F_{bc} T_{ac}^{ij} + F_{ac} T_{cb}^{ij}\right], \qquad (12)$$

$$\mathbb{M}^{1-\mathrm{h}} R_{ij}^{ab} = \cdots - \left[\sum_k T_{ab}^{ik} F_{kj} + T_{ab}^{kj} F_{ki}\right]$$

$$+ 0 \times \left[\sum_c F_{bc} T_{ac}^{ij} + F_{ac} T_{cb}^{ij}\right]. \qquad (13)$$

Application of $\mathbb{M}^{1-\mathrm{p}}$ or $\mathbb{M}^{1-\mathrm{h}}$ to $\mathbf{R}^X$ leads to a loss of the PH symmetry in the density matrices:

$$^{1-\mathrm{p}} D_{ab} = \sum_{ijc} \overline{T}_{ac}^{ij} T_{bc}^{ij} \quad {}^{1-\mathrm{p}} D_{ij} = 0, \qquad (14)$$

$$^{1-\mathrm{h}} D_{ij} = -\sum_{abk} \overline{T}_{ab}^{kj} T_{ab}^{ki} \quad {}^{1-\mathrm{h}} D_{ab} = 0. \qquad (15)$$

From Equations (14) and (15), it is evident that the trace of neither ${}^{1-\mathrm{p}}\mathbf{D}$ nor ${}^{1-\mathrm{h}}\mathbf{D}$ is zero, leading to the occurrence of spurious charges in the system.

The violation of particle-number conservation not only leads to artefacts in one-electron properties, but also to unphysical features in the correlation energy. Indeed, according to Equation (10), the one-electron density matrix directly affects the correlation energy. We investigate this effect using an example of hydrogen fluoride dimer, by computing the correlation contribution to the interaction energy using a PH symmetric method (for simplicity MP2) and the two variants that violate this symmetry given in Equations (12) and (13).

The corresponding potential energy curves (the correlation part thereof) are given in Figure 2 in the logarithmically scaled axes. According to Equation (10), the most slowly decaying component of the interaction energy comes from the electrostatic interaction between
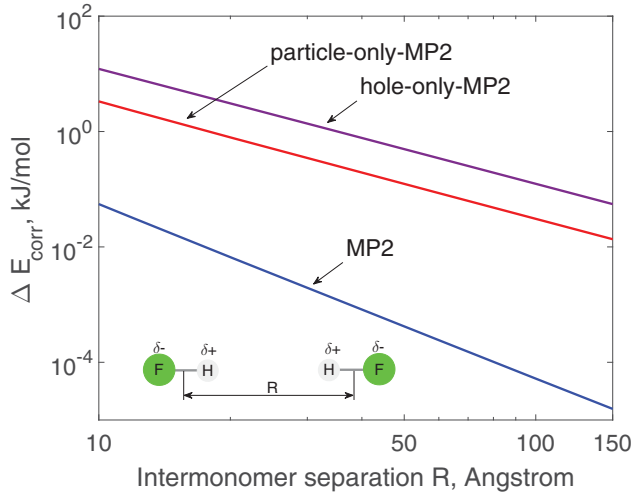
Figure 2. Correlation contribution to the interaction energy for the hydrogen fluoride dimer as a function of the intermonomer separation, computed by MP2, particle-only MP2 and hole-only MP2 methods, and cc-pVDZ basis set. Both axes are scaled logarithmically to linearise the decay-rate.

the correlated density and the HF density (appearing in the Fock matrix). For MP2, both densities are chargeless (the HF density appearing in the Fock matrix includes the compensating nuclear charges) leading to the R^{-3} decay with intermonomer separation R. However, if the PH symmetry is violated – as it is in Equations (12) and (13) – the correlated density matrix acquires spurious charges, leading to an unphysical R^{-2} decay. The erroneous decay properties are clearly visible in Figure 2.

2.3.3. Local particle–hole symmetry and the two-electron density matrix

To investigate the influence of the LPH symmetry on particle-number conservation in the two-electron density matrix, it is instrumental to consider the 'ladder' diagrams[2] of the CCD residual:

$$R_{ij}^{ab} \leftarrow \sum_{kl} T_{ab}^{kl}\left(ki|lj\right) + \sum_{cd} T_{cd}^{ij}\left(ac|bd\right)$$
$$- \sum_{kc} T_{cb}^{ik}\left(ac|kj\right) - \sum_{kc} T_{ac}^{kj}\left(ki|bc\right). \quad (16)$$

The first two terms, as well as the second two terms of Equation (16) separately are already PH symmetric. However, the LPH symmetry is guaranteed only if all four terms of Equation (16) are taken together.

The ladder diagrams of $\mathbf{R}^X$ involving a two-electron external perturbation can be related to the $^2D_{ik,jl}$, $^2D_{ca,db}$, $^2D_{ab,ij}$ and $^2D_{ij,ab}$ blocks of the two-electron density matrix. The explicit expressions for these contributions Δ^2D to the density matrix are

$$\Delta^2 D_{ik,jl} = \sum_{ab} \overline{T}_{ab}^{kl} T_{ab}^{ij}, \quad (17)$$

$$\Delta^2 D_{ac,bd} = \sum_{ij} \overline{T}_{ab}^{ij} T_{cd}^{ij}, \quad (18)$$

$$\Delta^2 D_{ab,ij} = -\sum_{kc} \overline{T}_{ac}^{kj} T_{bc}^{ki}, \quad (19)$$

$$\Delta^2 D_{ij,ab} = -\sum_{ij} \overline{T}_{ca}^{jk} T_{cb}^{ik}. \quad (20)$$

We consider now the partial traces of $\Delta^2 D$ associated with each of the two electrons:

$$\sum_i \Delta^2 D_{ii,jk} + \sum_a \Delta^2 D_{aa,jk}, \quad (21)$$

$$\sum_i \Delta^2 D_{ii,bc} + \sum_a \Delta^2 D_{aa,bc}, \quad (22)$$

$$\sum_i \Delta^2 D_{jk,ii} + \sum_a \Delta^2 D_{jk,aa}, \quad (23)$$

$$\sum_i \Delta^2 D_{bc,ii} + \sum_a \Delta^2 D_{bc,aa}. \quad (24)$$

In contrast to the 'excitonic' terms of the type $\sum_{kc} T_{cb}^{kj}\left(ki|ac\right)$, which describe the interaction between an electron and its own hole, the ladders correspond to the interaction between two separate particles or holes. Therefore, particle-number conservation demands that all partial traces in Equations (21)–(24) are zero, and this is only possible if all four blocks in Equations (17)–(20) appear in the two-electron density matrix.

If now in an approximate theory, $\mathbb{M}$ removes some (but not all) ladder diagrams from Equation (16), thus eliminating LPH symmetry, some of the density-matrix contributions (21)–(24) will be missing and hence, at least some of the traces in Equations (17)–(20) will no longer be zero. This will again introduce spurious charges in the two-particle density, causing unphysical artefacts in the two-electron part of the interaction.

To illustrate this effect, we have plotted contributions to the MP3 interaction energy $\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$ arising from individual ladder contributions:

$$E_{\text{hh}} = \sum_{ab} \sum_{ijkl} \overline{T}_{ab}^{ij} T_{ab}^{kl}\left(ki|lj\right), \quad (25)$$

$$E_{\text{pp}} = \sum_{abcd} \sum_{ij} \overline{T}_{ab}^{ij} T_{cd}^{ij}\left(ac|bd\right), \quad (26)$$

$$E_{\text{ph}} = -\sum_{abc} \sum_{ijk} \left[\overline{T}_{ab}^{ij} T_{cb}^{ik}\left(ac|kj\right) + \overline{T}_{ab}^{ij} T_{ac}^{kj}\left(ki|bc\right)\right].$$
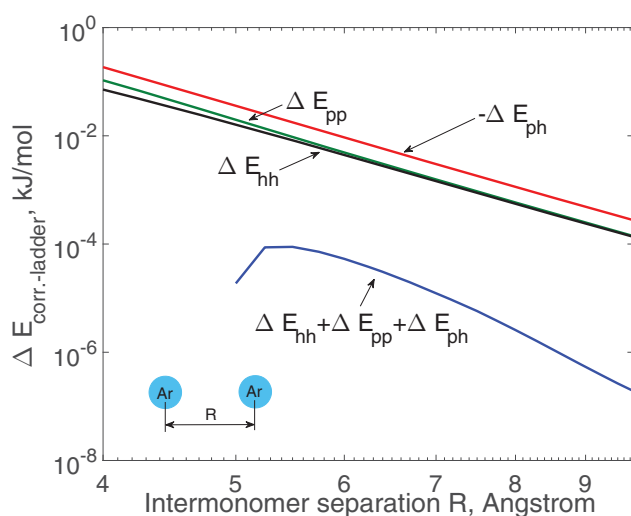$$(27)$$

Figure 3. The counterpoise corrected ladder-diagram contributions to the MP3 interaction energy for an argon dimer as a function of the interatomic separation. The aug-cc-pVTZ basis set was used. Both axes are scaled logarithmically to linearise the decay-rate.

The values are shown for an argon dimer as a function of interatomic distance in Figure 3. Both $\mathbf{T}$ and $\overline{\mathbf{T}}$ are the MP2 amplitudes here, since, due to the symmetry of the Hylleraas functional, the MP2 Lagrange multipliers are identical to the amplitudes.

The decay properties of these terms can be rationalised in the local orbital basis. If the orbitals are localised on the two monomers, the corresponding components of the two-electron density matrix asymptotically decay as R^{-6} with intermonomer distance. The Coulomb interaction between the respective densities accelerates this decay further. If the densities contain spurious charges, the additional factor is only R^{-1} and the overall asymptotic decay is R^{-7}. This is exactly the decay of the individual ΔE_{hh}, ΔE_{pp} and ΔE_{ph} terms seen in Figure 3. However, the physically correct densities are chargeless, which correspond to at least an R^{-9} decay [24–28]. Indeed, in Figure 3, the sum of the terms E_{hh}, E_{pp} and E_{ph}, which is LPH symmetric and corresponds to physically correct densities, decays much faster.

As a side note: the rapid decay of the sum of the ladder energy contributions allows for neglect of all four ladder terms for intermolecular pairs in local CC methods, providing substantial computational savings [25,26].

3. Conclusion

When electron correlation methods are constructed on the basis of an anti-symmetric model wavefunction, symmetries intrinsic in the second-quantised operators for fermions are carried over to the resulting method: particle–hole symmetry and local particle–hole

symmetry are guaranteed in diagrammatic methods; and typically, methods that are exact for a given number of particles are also exact for the same number of holes.

In CC methods, density matrices are usually constructed through a response formalism, although this leads to non-n-representable density matrices. Even so, one of the most important requirements of n-representability is satisfied: that the traces of the one- and two-particle density matrices are equal to the number of particles or of pairs of particles.

In CC-like methods that do not have an explicit form for the wavefunction, there is no option but to compute density matrices in a response formalism. And here, the lack of connection to a properly anti-symmetrised state can lead to more severe errors in n-representability. As we have seen, when methods are constructed that satisfy LPH symmetry, at least the traces of the one- and two-particle density matrices are guaranteed to be correct. Violation of this property is not a side issue that arises only for property evaluation, but instead directly impacts on the computation of correlation energies.

It is possible to construct methods that do not satisfy LPH, but do produce density matrices with the correct traces, and pCCSD provides an important example of this type of theory. However, it is possible that the lack of LPH symmetry leads to other defects in the theory that are less easily detectable. There is some evidence of this possibility: in the pCCSD(μ, 1) family of methods with $\mu < 0$, the hole-Fock-type mosaic diagram is scaled-down (increasingly as μ becomes more negative) while the particle analogue remains unchanged. One interpretation of this is that the screening between particles is not balanced with the screening between holes, and one can expect a lowering of the excitation energy as μ is lowered. This agrees perfectly with the findings for equation-of-motion-pCCSD: 'as the parameter changes from $\mu = 0$ to -1.5, we find that the excitation energies (for single excited states) decrease fairly systematically' [29]. We will investigate the connection between the particle–hole symmetry and the conservation of the number of 'quasi-particles', that intrinsically include screening effects, in a forthcoming publication.

Finally, it is worth noting that when the distinguishable cluster approximation was developed [15,17,20], local particle–hole symmetry was used as a design criterion. It may be that the surprising accuracy of the approach arises in part as a consequence of this choice.

Notes

1. In quantum chemistry, it is common to use a third alternative, the particle–hole formalism, in which determinants are produced by creating pairs of particles and holes in a

Fermi vacuum, and we adopt this more conventional formalism in what follows. We use the conventional notation for spin-orbital indices such that $i, j, \ldots$ denote occupied; $a, b, \ldots$ denote virtual; and $p, q, \ldots$ denote arbitrary spin-orbitals.

2. Conventionally, only the first two terms in Equation (16) are referred to as ladder diagrams. However, since the four diagrams of Equation (16) are interrelated by the LPH symmetry, for convenience we apply the term 'ladder diagram' to all of them.

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Disclosure statement

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