Symmetry-restricted functionals in one-body reduced density matrix functional theory

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In many of the approximate functionals in one-body reduced density matrix (1RDM) functional theory, the approximate two-body reduced density matrix (2RDM) in the natural orbital representation only depends on the natural occupation numbers. In Phys. Rev. A 92, 012520 (2015) Wang and Knowles initialised the discussion to which extend this simplification is valid, by introducing two different $\text{H}_4$ geometries with identical natural occupation numbers, but different 2RDMs. Gritsenko has argued that this feature is due symmetry dependence of the exact functional [Phys. Rev. A 97, 026501 (2018)]. This work aims to contribute to the discussion on the following points: 1) the feature that the exact functional can yield different 2RDMs for the same set of natural occupations can be explained without symmetry, so is more general; 2) the exact functional is not symmetry dependent, though it is possible to define symmetry-restricted variants of the exact functionals; 3) symmetry-restricted functionals are derived for the $\text{H}_4$ geometries considered by Wang and Knowles, which can serve as guide in the construction of approximate 1RDM functionals.

I. INTRODUCTION

In Ref. [1] Wang and Knowles have given an example in which two one-body reduced density matrices (1RDMs) with identical natural occupation spectra correspond to two different ground state two-body reduced density matrices (2RDMs). This is a feature that most common approximate 1RDM functionals cannot handle, since they generate an approximate 2RDM via an explicit algebraic expression. Wang and Knowles argued that a functional dependence on the natural orbitals (eigenfunctions of the 1RDM) also needs to be included in the approximations, if approximate 1RDM functionals aim to handle these isospectral cases correctly.

In his Comment [2], Gritsenko used the constrained-search formulation of 1RDM functional theory [3, 4] in an attempt to explain more clearly how the exact functional differentiates 1RDMs with identical occupation numbers, but different natural orbitals (NOs). Since the example by Wang and Knowles compared two systems with different symmetry properties, Gritsenko inferred that the exact functional would need to be symmetry dependent. He proposed to decompose the constrained-search functional as a minimisation of all possible symmetry groups. In their Reply [5], Wang and Knowles argued that symmetry dependence cannot be the answer for their demonstration, since they could easily destroy the symmetry of their systems, while still obtaining 1RDMs with identical occupation numbers. I will show that indeed no symmetry is needed to explain the results by Wang and Knowles [1] and that their results can directly be understood from the definition of the constrained-search functional.

The idea of imposing symmetry restrictions on the universal functional can still be useful. Though such a symmetry-restricted functional is only exact for systems with the assumed symmetry, the advantage is that the variational freedom in the constrained-search formulation is significantly reduced. This allows one to build explicit parametrisations of these functionals for simple systems, which can serve as a guide for the construction of approximate functionals. In this article I will construct two different symmetry-restricted functionals valid for the square $\text{H}_4$ system and $\text{H}_2 + 2\text{H}$ in a minimal basis; the systems used in the demonstration by Wang and Knowles [1]. These are exactly functionals of the type desired in Refs [5] and [6]: both functionals are symmetry restrictions of the exact functional, though still flexible enough to deal with both $\text{H}_4$ systems.

The article is organised as follows. In Sec. II different formulations of the exact functional are discussed and how the results by Wang and Knowles [1] can directly be rationalised from the constrained-search formulation. In Sec. III symmetry restrictions of the universal 1RDM functional are discussed and it is demonstrated the true universal functional cannot be considered to be symmetry dependent. In Sec. IV the two relevant components (irreducible representations) of the symmetry-restricted $D_{2h}$ functional are constructed for the $\text{H}_4$ systems in a minimal basis. The parametrisation of the totally symmetric component of the more general $C_{2v}$ functional is constructed in Sec. V. In Sec. VI I finalise with the conclusions.

II. EXACT FUNCTIONALS

There are two different exact interaction energy functionals one could consider. Both are exact in the sense that both yield the exact ground state interaction energies, but they differ in their mathematical properties. Most notable are their different domains and convexity properties.
The first exact 1RDM functional useful for our purposes was proposed by Levy [3]  
\[ W_L[\gamma] := \min_{\Psi \to \gamma} \langle \Psi | \hat{W} | \Psi \rangle, \]  
(1)  
where \( \hat{W} \) denotes the interaction operator. The constrained search only runs over pure states, which has the disadvantage that its domain is difficult to characterise, i.e. the so-called pure state \( N \)-representable 1RDMs [7–9]. To this end, Valone proposed to extend the search over mixed states [4]  
\[ W_V[\gamma] := \min_{\hat{\rho} \to \gamma} \text{Tr} \{ \hat{\rho} \hat{W} \}, \]  
(2)  
where \( \hat{\rho} \) denotes the (full) density-matrix operator and the trace runs over the full Hilbert / Fock space. The advantage is that the domain is now the enlarged and more convenient set of ensemble \( N \)-representable 1RDMs [10]. An additional advantage is that this functional is convex by construction \[ \text{An additional advantage is that this functional is convex in physicist notation and the 2RDM is defined as} \]  
\[ \Gamma_{ij,kl} = \langle \hat{\rho} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l | \Psi \rangle \]  
(3)  
where we use the same notation as Wang and Knowles [1], i.e., \( \langle ij|kl \rangle \) are the two-electron integrals in physicist notation and the 2RDM is defined as \( \Gamma_{ij,kl} = \langle \Psi | \hat{\rho} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l | \Psi \rangle \) for pure states and \( \Gamma_{ij,kl} = \text{tr} \{ \hat{\rho} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l \} \) for the more general mixed states. The minimisation should only search over pure (Levy) or ensemble (Valone) \( N \)-representable 2RDMs, to ensure that a corresponding pure or mixed state exists which yields this 2RDM and hence, that the variational principle applies.

Note that any one-particle basis can be used in this form of the universal functional. We can use this freedom to simplify the constraint on the 2RDMs by working in the natural orbital (NO) basis of the requested 1RDM [14]. As the 1RDM is diagonal by definition, the constraint on the 2RDM reduces to  
\[ \sum_j \Gamma_{ij,kj} = (N-1)n_i \delta_{ik}, \]  
(4)  
where \( n_i \) are the natural occupation numbers, i.e. eigenvalues of the 1RDM.

This means that if we transform the two-electron integrals to the NO-basis, the constrained search only needs to know about the occupation numbers  
\[ W[\gamma] = \frac{1}{2} \min_{\xi} \sum_{ijkl} \Gamma_{ij,kl} \langle i j | k l \rangle_{\text{NO}}, \]  
(5)  
Under the assumption that we are able to find some suitable parametrisation \( \xi \) of the set of \( N \)-representable 2RDMs yielding the requested occupation number spectrum \( \Gamma_{ij,kl}[\xi, n] \), we can also express the functional as the minimisation over parameters \( \xi \) [14]  
\[ W[\gamma] = \frac{1}{2} \min_{\xi} \sum_{ijkl} \Gamma_{ij,kl}[\xi, n] \langle i j | k l \rangle_{\text{NO}}. \]  
(6)  
Note that the parametrisation \( \Gamma_{ij,kl}[\xi, n] \) only needs to know about the occupation numbers and not the NOs, since \( N \)-representability does not depend on the orbital basis [10]. It should be obvious that such a parametrisation in terms of \( \xi \) is definitely not unique. There are only convenient and less convenient parametrisations, depending on the situation.

In principle, the route towards construction of such an explicit functional is straightforward: 1) write down a parametrisation of the wavefunction or the density-matrix operator in the NO basis, 2) eliminate parameters that are determined by the 1RDM constraint 3) and finally contract the wavefunction / density-matrix operator to the 2RDM. Unfortunately, the 1RDM constraint enters in a non-linear way, which makes the elimination of parameters a non-trivial task in practice. Especially the positivity constraint of the density-matrix operator are difficult to conciliate with the 1RDM constraint. The Valone functional (2) has therefore only been explicitly constructed for a two-site Anderson model [15].

Working with a constrained search over only pure states (1) is more convenient for an explicit construction. Such an explicit construction is readily possible for the two-electron case, thanks to the Schmidt decomposition [16] (sometimes referred to as the Carlson–Keller expansion [17]), which makes the constraint \( \Psi \to \gamma \) trivial. The anti-symmetry requires the NOs \( \phi_k(x) \) to be pairwise degenerate [10]: \( n_k = n_{-k} \). The wavefunction can now be expressed as  
\[ \Psi(x_1, x_2) = M \sum_{k=1}^M \sqrt{n_k} e^{i \xi_k} | \phi_k(x_1) \phi_{-k}(x_2) \rangle, \]  
(7)  
where \( \mathbf{x} = r \sigma \) is a combined space-spin coordinate and \( 2M \) is the amount of spin-orbitals in the basis [20]. The 2RDM is readily found to be  
\[ \Gamma_{ij,kl}[\xi, n] = \sqrt{n_i n_k} e^{i (\xi_e - \xi_i)} \delta_{i,-j} \delta_{k,-l}, \]  
(8)  
with \( \xi_{-k} = \xi_k + \pi \). The free parameters \( \xi \) in the exact two-electron functional are the phases in the two-electron wavefunction (7), which are the only degrees of freedom not fixed by the 1RDM.

Wang and Knowles actually dismiss such a form of the exact functional, which houses internally an additional variable set \( \xi \): “One may take the phase as additional variables [21], then this will go beyond Gilbert’s original variable set: the natural orbitals and their occupation numbers.” One has to keep in mind, however, that all density-functional-like theories are actually reformulations of the Schrödinger equation. This means that
the full flexibility of the complete many-body state cannot magically disappear and needs to be accounted for somewhere in the theory. Levy’s constrained-search formulation makes this very explicit by minimising over all pure states (1) or in the extension by Valone, which also searches over mixed states (2). This additional variational freedom beyond degrees of freedom of the 1RDM persists of course when we reformulate the exact functional as a search over $N$-representable 2RDMs (3) and is made explicit as the variable set $\xi$ in (6).

The additional variational freedom in the exact functional is actually the crucial property to explain the results presented by Wang and Knowles in Ref. [1]. Though the occupation numbers can be made identical in both systems (square $H_4$ and $H_2 + 2\mathbf{h}$), the NOs are different and hence, lead to a different set of two-electron integrals in (6). As the two-electron integrals have different values, the minimisation over the variables $\xi$ will lead to a different minimum and thus, a different 2RDM.

It might be that Wang and Knowles have a different functional form of the 2RDM in mind. Since every observable can be regarded as a functional of the 1RDM in 1RDM functional theory [22], or equivalently, as a functional of the NOs and occupation numbers $\Gamma^{NO}[\{\phi\}, n]$. This is the functional aimed for by many approximate functional developers, since in that case the interaction energy is directly given as

$$W[\{\phi\}, n] = \frac{1}{2} \sum_{ijkl} \Gamma^{NO}[\{\phi\}, n]_{ijkl} \langle ij|kl|\rangle_{NO} \quad (9)$$

which does not contain an internal optimisation. The disadvantage is that the functional dependence of $\Gamma^{NO}[\{\phi\}, n]$ is more complicated than $\Gamma[\xi, n]$; even for simple systems, no explicit form of $\Gamma^{NO}[\{\phi\}, n]$ is known. Both functionals are related as

$$\Gamma^{NO}[\{\phi\}, n] = \arg \min_{\Gamma \rightarrow n} \sum_{ijkl} \Gamma_{ijkl} \langle ij|kl|\rangle_{NO}$$

$$\Gamma[\xi, n] = \Gamma[\xi_{opt}, n], \quad (10)$$

where $\xi_{opt}$ are the optimising parameters in (6). So the NO dependent variant can be obtained by performing the minimisation over the parameters $\xi$ in (6) [or the constraint search in (5)] and then the 2RDM elements can be extracted. This implicit dependence of $\Gamma^{NO}[\{\phi\}, n]$ on the NOs makes it inconvenient to build approximations which try to capture this NO dependence directly. Exact constructions of $\Gamma_{ijkl}[\xi, n]$ are more feasible and therefore provide a better starting point for approximate 1RDM functionals that aim to go beyond a simple dependence on the natural occupation numbers.

It is worth to point out that relation (10) implies that the functional dependence on the NOs of the 2RDM only vanishes, if also $\Gamma_{ijkl}$ only depends on the occupation numbers. In this case, these functionals are even equal

$$\Gamma^{NO}_{ijkl}[n] = \Gamma_{ijkl}[n], \quad (11)$$

However, such a simple form can never occur for the exact functional, except in very limited settings, e.g. two electrons in two orbitals. The alleged simple dependence $\Gamma_{ijkl}[n]$ in Ref. [6] for two-electron systems [23] and translationally invariant one-band lattice models [24] is actually incorrect. For the two-electron system, we have an internal optimisation over phase factors (8) and translationally invariant one-band lattice models the internal minimisation is actually clearly mentioned just after Eq. (9) in Ref. [24]. A desired exact functional by Gritsenko et al. for the rhombus $H_4$ system in Ref. [6] will be given in Sec. IV, but is clearly not of the simple form $\Gamma_{ijkl}[n]$.

### III. SYMMETRY RESTRICTIONS

The pure-state expression for the 2RDM of two-electron systems (8) is completely general, valid for any spin-dependent potential and spin-dependent two-electron interaction. However, often we work with the spin-independent Coulomb interaction and spin-independent potentials (no magnetic fields). This means that the Hamiltonian commutes with the spin-operators and the eigenstates can be classified according to their spin-state. The constrained search can therefore be restricted to either singlet or triplet states as originally done by Löwdin and Shull [23]. They additionally used that the Hamiltonian is now also real, so the eigenstates can be chosen to be real and hence, the phase factors $e^{i\xi_f} = \pm 1$.

Let us put this in a more general setting. In case we are only interested in external potentials / Hamiltonians with a certain symmetry, we know that the ground state will belong to one of the irreducible representations (irreps) of the symmetry group. The constrained search can therefore be broken down into separate constrained searches over each irrep $I$ of the symmetry group $S$

$$W^S[\gamma] := \min_{I \in S} W^I_S[\gamma], \quad (12a)$$

where

$$W^I_S[\gamma] := \inf_{\Psi \rightarrow \gamma} \langle \Psi | W | \Psi \rangle$$

$$= \frac{1}{2} \inf_{\xi} \sum_{ijkl} \Gamma_{ijkl}[I, \xi, n] \langle ij|kl|\rangle_{NO}. \quad (12b)$$

In the definition of $W^I_S[\gamma]$ we have put an infimum, since it is well possible that no $\Psi \rightarrow \gamma$ can be found, in which case we set $W^I_S[\gamma] = +\infty$.

These symmetry-restricted functionals can either be considered exact or approximate depending on the viewpoint.

1. If we restrict ourselves to all potentials which have the symmetry $S$, $W^S[\gamma]$ is an exact functional in the sense that for all ground-state 1RDMs of that
symmetry group, it will yield the exact ground state interaction energy. So this can be regarded as a restriction in the universality of the functional, with a corresponding adaptation of the domains.

2. Alternatively we do not alter the set of potentials. If the external potential happens to belong to the symmetry group \( S \), the symmetry-restricted functional will yield the exact interaction energy, otherwise it only yields an upper bound, since obviously we have \( W_S^\gamma \geq W_L[\gamma] \). It might even be that no \( \Psi^I \rightarrow \gamma \) exist, in which case we need to set \( W_S^\gamma = +\infty \). So in this viewpoint we should even replace the min by an inf in (12a). To summarise in this viewpoint, a symmetry-restricted functional is an approximation to the exact universal functional (1).

The physical exception is the particle number. Typically we work with particle conserving interactions, e.g. the Coulomb interaction. Since the non-local potential is by definition particle conserving, the particle number will always commute with the Hamiltonian, so will always be a symmetry of the system and the ground state has an integer particle number. Additionally, because the ionisation potential is always larger than the electron affinity, the constrained-search functional will always prefer an \( N \)-electron state over an equal mix of an \((N-1)\)- and \((N+1)\)-electron state. Specialising (12) to the particle number symmetry, we have

\[
W^\#_N[\gamma] = \min_{\gamma \in \mathbb{N}} W^\#_N[\gamma] \tag{13a}
\]

\[
W^\#_N[\gamma] = \inf_{\Psi^N \rightarrow \gamma} \langle \Psi^N | \hat{W} | \Psi^N \rangle \tag{13b}
\]

Since \( W^\#_N[\gamma] < \infty \) only if \( \text{tr}\{\gamma\} = N \), only this irrep yields a candidate for the minimum

\[
W^\#[\gamma] = \min_{\Psi^\text{tr}\{\gamma\}} \langle \Psi^\text{tr}\{\gamma\} | \hat{W} | \Psi^\text{tr}\{\gamma\} \rangle. \tag{14}
\]

The parametrised 2RDM for the 2 particle case (8) yields the 2 particle sector of this form of the exact functional. The 1 particle sector is trivial \((W^\#_1[\gamma] = 0)\) and for more than 2 particles explicit general expressions are unknown.

Gritsenko argued that symmetry-restricted functionals would give an explanation that different 2RDMs can correspond to an identical occupation number spectrum [2]. In an attempt to recover the exact functional he proposed to minimise over all symmetry classes (Eq. (3) in [2]), but obviously all systems belong to the “no-symmetry” group which is simply the Levy-constrained-search functional (1)

\[
\min_S W^S[\gamma] = W^{\text{no sym}}[\gamma] = W_L[\gamma]. \tag{15}
\]

So a search over symmetry groups is pointless, since the constrained search with no symmetry is identical the full Levy constrained search (1). Thus symmetry does not provide any explanation that different 2RDMs can correspond to identical occupation numbers [1]. Instead, we can resort to the simple argument presented in Sec. II, which is completely sufficient and does not make any reference to symmetry.

Gritsenko’s confusion is probably caused by the high symmetry of the examples by Wang and Knowles, so examples without symmetry might have been more appropriate. However, the high symmetry is actually useful to make the analysis of the wavefunction and the corresponding 2RDM and 1RDM more manageable and transparent. This is actually an important reason why it would still be useful to consider symmetry-restricted functionals. Though limited in their validity, their construction is more feasible, since the number of terms in the CI expansion can be significantly reduced.

Let us consider the explicit construction in some more detail. Assuming that the wavefunction is expanded in NOs, the constrained search (1) imposes two types of conditions: 1) diagonality conditions, i.e. that the 1RDM is diagonal and 2) occupation number conditions. The conditions from the occupation numbers do not contain any cross terms between the configurations, so these conditions lead to a set of linear constraints on the square modulus of the CI coefficients

\[
\sum_I A_{kI} |c_I|^2 = n_k, \tag{16}
\]

where \( I \) runs over the configurations and \( A_{kI} \) tells how much each configurations \( I \) contributes to the natural occupation \( n_k \). This linear set of equations is easily solved to determine the constraints on the CI coefficients and the null-space of \( A \) yields the remaining variational freedom, i.e. parameters \( \xi \) in (6), apart from the phase of the CI coefficients. This is exactly how the exact functional for the translationally invariant one-band lattice models were constructed [24].

On the other hand, the diagonality conditions do mix different configurations, so these conditions contain products of different CI coefficients. Hence, the presence of these conditions leads to coupled quadratic equations, which are difficult to solve in general. Although, for simple cases like the examples put forward by Wang and Knowles, it is still possible to solve these equations (see Sec. IV) when there are only a few diagonality constraints.

### IV. THE \( D_{2h} \) SYMMETRY-RESTRICTED FUNCTIONAL FOR THE \( H_4 \) SYSTEMS IN MINIMAL BASIS

In this section we construct symmetry-restricted functionals for the square \( H_4 \) and \( H_2 \) + 2H systems studied by Wang and Knowles in a minimal 1s basis [1]. The most general Levy-type functional for these systems would need to deal with 4 electrons in 8 spin-orbitals, i.e. a configuration interaction (CI) expansion of \( (8)_4 = 70 \)
terms. However, when using full spin-symmetry, we only need to deal with 20, 15, 1 configuration state functions for the singlet, triplet and quintet irreps respectively.

Gritsenko considered the \( H_2 + 2H \) system to be arranged in a trapezoid [2], with the shorter of the two parallel sides being the \( H_2 \) bond and the longer side tending to infinity. The square \( H_4 \) system can be regarded as a trapezoid with parallel legs. This allows us to use the \( C_{2v} \) symmetry group as a common symmetry group for both systems. In this case both systems have their ground state in the \( 1^{1}A_1 \) irrep, which has 12 terms in its expansion. One can actually construct a parametrisation for this wave function, because there are only two conditions to make the corresponding 1RDM diagonal. The construction of this parametrisation is quite involved, so will be postponed till Sec. V. In this section, we will use a higher symmetry group, which makes the construction less complicated and more instructive to get the general idea.

As observed in Ref. [6], the highest common symmetry group is actually \( D_{2h} \), if we arrange the \( H_2 + 2H \) system in a rhombus instead of a trapezoid. The \( H_2 \) bond is then placed along the short diagonal and the long diagonal of the rhombus tends to infinity. The square \( H_4 \) is simply a rhombus in which the diagonals have equal length. In this case the ground state of the \( H_2 + 2H \) system belongs to the \( 1^{1}A_g \) irrep, whereas the ground state of the square \( H_4 \) system belongs to the \( 1^{1}B_{1g} \) irrep. We therefore need to construct the symmetry-restricted functional in two irreps, though these are two easier tasks, since the wavefunctions in these irreps only contain 8 and 4 terms respectively. But more importantly, we only need to handle one diagonality constraint.

Let us consider first the simpler \( 1^{1}B_{1g} \) irrep in detail. A general wavefunction in this irrep can be written as [25]

\[
\Psi^{1^{1}B_{1g}} = c_1 |1a_g^2b_2u^3a_3u| + c_2 |2a_g^2b_2u^3a_2b_3a| + c_3 |1a_g2a_gb_2u^3a_3b_3a + \alpha\beta\alpha + \beta\alpha\beta - 2(\alpha\alpha\beta + \beta\beta\alpha)| + c_4 |1a_g2a_gb_2u^3a_3b_3a - \alpha\beta\alpha - \beta\alpha\beta + 2(\alpha\alpha\beta + \beta\beta\alpha)|. \tag{17}
\]

This wavefunction can only yield spin-integrated 1RDMs with \( n_{b_2u} = n_{b_3u} = 1 \) and \( n_{a_g} + n_{a_{2g}} = 2 \), so only for those 1RDMs \( \Pi^{D_{2h}}_{1^{1}B_{1g}} < \infty \).

To construct a parametrisation, we first observe that the 1RDM has 2 orbitals in the \( a_g \) block, 1 orbital in the \( b_{2u} \) block and 1 orbital in the \( b_{3u} \) block, so we only need to make the 1RDM diagonal in the \( a_g \) block. The off-diagonal element of the 1RDM from \( \Psi^{1^{1}B_{1g}} \) vanishes if \( c_4(c_1 + c_2) = 0 \). Since \( c_1 + c_2 = 0 \) is only possible if \( n_{1a_g} = n_{2a_g} \), which is unlikely due to the higher kinetic energy of \( n_{2a_g} \), we only parameterise for \( c_4 = 0 \), which is in agreement with the higher \( D_{4h} \) symmetry of the square \( H_4 \) [1, 6]. The remaining degrees of freedom can be parametrised with one parameter \( \xi_1 = c_1 + c_2 \). From the intermediate result

\[
\xi_2 = c_1 - c_2 = \frac{n_{1a_g} - n_{2a_g}}{4\xi_1}, \tag{18}
\]

the CI coefficients can now readily be calculated as

\[
c_1 = (\xi_1 + \xi_2)/2, \tag{19a}
\]
\[
c_2 = (\xi_1 - \xi_2)/2, \tag{19b}
\]
\[
c_3 = \frac{1}{4\xi^3}(1 - \xi^2 - \xi_2^2)^{1/2}. \tag{19c}
\]

Since we have the CI coefficients now as a function of \( \xi_1 \), we also have the 2RDM elements \( \Gamma^{D_{2h}}_{ij,kl}[1^{1}B_{1g}, \xi_1, \mathbf{n}] \), which are in principle the ones given in [6], except that there is an error in the opposite-spin-block of the 2RDM for square \( H_4 \) Eq. (22). The columns and rows of 22 and 33 should be empty, since these terms never occur in the wavefunction. The correct symmetry blocked 2RDM has been deferred to Appendix A, as it is rather unwieldy and not useful for the discussion at this point.

The ground state of the \( H_2 + 2H \) system belongs to the \( 1^{1}A_g \) irrep for which the expansion becomes

\[
\Psi^{1^{1}A_g} = c_1 |1a_{g2}b_{2u}^2| + c_2 |2a_{g2}b_{2u}^2a_{2b}| + c_1 |2a_{g2}b_{2u}^3a_3b_3a| + c_3 |1a_{g2}b_{2u}^3a_3b_3a + \alpha\beta\alpha + \beta\alpha\beta - 2(\alpha\alpha\beta + \beta\beta\alpha)| + c_4 |1a_{g2}b_{2u}^3a_3b_3a - \alpha\beta\alpha + \beta\alpha\beta + 2(\alpha\alpha\beta + \beta\beta\alpha)|, \tag{20}
\]

Because there are more terms, constructing a parametrisation becomes more tedious. Since there are 8 terms in the wavefunction and the 1RDM yields 5 non-trivial conditions (4 occupation numbers and 1 non-trivial off-diagonal element in the \( a_g \) block), we expect that we need at least 3 parameters.

In order for this wavefunction to yield a diagonal 1RDM, we need to satisfy the following condition

\[
0 = (c_1^b + c_2^b)(c_{12}^{ab} + c_{23}^{ab} + c_{22}^{ab} + c_{22}^{ab}) + (c_1^b - c_2^b)(c_{12}^{ab} - c_{23}^{ab} + c_{22}^{ab} - c_{12}^{ab}). \tag{22}
\]

The advantage of this form is that we can now eliminate \( c_{11}^{ab} - c_{22}^{ab} \) and \( c_{11}^{ab} - c_{22}^{ab} \) in favour of the other terms, by exploiting the following two conditions put by the occupation numbers on the coefficients

\[
\Delta_+ = |c_{11}^{ab}|^2 - |c_{22}^{ab}|^2 + |c_{12}^{ab}|^2 - |c_{22}^{ab}|^2, \tag{23a}
\]
\[
\Delta_- = |c_{11}^{ab}|^2 - |c_{22}^{ab}|^2 + |c_{22}^{ab}|^2 - |c_{12}^{ab}|^2, \tag{23b}
\]

where

\[
\Delta_\pm = (n_{1a_g} - n_{2a_g} \pm n_{b_2u} \mp n_{b_3u})/4. \tag{24}
\]
Introducing the following parametrisation for the coefficients,
\[ \xi_1 = c_{11ab} + c_{22ab}, \quad \xi_2 = c_{12ab} + c_{21ab}, \quad \xi_3 = c_1 - c_2, \]
the diagonality condition (22) yields an explicit equation for \( c_1 + c_2 \)
\[ \zeta_4 = c_1 + c_2 = \frac{\xi_1}{\xi_1 + \xi_2} \frac{\Delta_+ - \Delta_-}{\xi_1 \xi_2 - \xi_3^2}. \] (26a)

From the conditions (23) themselves we can extract
\[ \zeta_5 = c_{11ab} - c_{22ab} = (\Delta_+ - \xi_3 \zeta_4) / \xi_1, \] (26b)
\[ \zeta_6 = c_{12ab} - c_{21ab} = (\Delta_- + \xi_3 \zeta_4) / \xi_2. \] (26c)

The normalisation condition of the wavefunction, or equivalently the trace of the 1RDM, yields
\[ \zeta_7 = |c_{12}^{ab}|^2 + |c_{12}^{bb}|^2 = 1 - \zeta_3^2 - \zeta_4^2 - \frac{1}{2} (\zeta_1^2 + \zeta_2^2 + \zeta_5^2 + \zeta_6^2) \] (26d)
and there is one additional independent linear combination of occupation numbers, which yields the relation
\[ \zeta_8 = |c_{12}^{ab}|^2 - |c_{12}^{bb}|^2 = \Delta_0. \] (26e)
where
\[ \Delta_0 = (n_{1ga} + n_{2ga} - n_{bga} - n_{bga}) / 4 \] (27)
The CI coefficients are obtained as
\[ c_{11ab}^{ab} = (\xi_1 + \zeta_5) / 2, \quad c_{22ab}^{ab} = (\xi_1 - \zeta_5) / 2, \] (28a)
\[ c_{12ab}^{ab} = (\xi_2 + \zeta_6) / 2, \quad c_{21ab}^{ab} = (\xi_2 - \zeta_6) / 2, \] (28b)
\[ c_1^{ab} = (\xi_3 + \zeta_4) / 2, \quad c_2^{ab} = (\xi_3 - \zeta_4) / 2, \] (28c)
\[ c_{12}^{aa} = \sqrt{\zeta_7 + \zeta_8}, \quad c_{12}^{bb} = \xi_1 \sqrt{\zeta_7 - \zeta_8}, \] (28d)
where we needed to introduce one additional parameter \( \xi_4 = \pm 1 \) to handle the unknown relative phase factor. Since the exact form of the 2RDM is not particularly enlightening, it is not presented here, but still reported in Appendix B for completeness.

It might seem to be a contradiction that we still have 4 free parameters for the \( \text{H}_2 + 2 \text{H} \) system, since Grisanko et al. in Ref. [6] did not find additional parameters. The difference is that we only used symmetry to build a specialised functional. However, if we also use the special property of the \( \text{H}_2 + 2 \text{H} \) system that the Coulomb integrals between the fragments disappear, the minimisation in (12b) can be executed explicitly (see Appendix C) and we recover the result by Grisanko et al. [6]: a one-to-one relation between the 2RDM elements and the occupation numbers.

At this point it should be mentioned that such additional assumptions are often made to develop approximations. We actually made such an assumption \( (c_4 = 0) \) for \( T_D^{2k} \) to simplify the final expression. A similar assumption is well known for the singlet two-electron case, where the phase \( e^{i \phi} \) is taken to be positive for the highest occupied NO and negative for all other NOS [26]. However, this additional assumption reduces the validity of the two-electron functional as it is not exact anymore for all singlet two-electron cases. Though the covalent bonding is still correctly described, the Van der Waals interactions are missing [27-29].

V. THE \( C_{2v} \) SYMMETRY-RESTRICTED FUNCTIONAL FOR THE \( \text{H}_2 \) SYSTEMS IN MINIMAL BASIS

There are only two relevant irreps to consider: \( a_1 \) and \( b_1 \) (or \( b_2 \) depending on the axis system), because the basis consists only of 1s-orbitals localised on the hydrogen atoms. We label symmetry adapted and orthonormalised spatial orbitals as
\[ \{1_a, 2_a, 1_b, 2_b\}. \] (29)

We can use these symmetry adapted orbitals to construct the following full CI expansion for a general \( 1A_1 \) state
\[ \Psi^{A_1} = c_{11}^{ab} |1_a^2 2_b^2 \rangle + c_{21}^{ab} |2_a^2 1_b^2 \rangle + c_{12}^{bb} |1_a^2 1_b^2 \rangle + c_{22}^{ab} |2_a^2 2_b^2 \rangle + c_{11}^{ab} |1_a 2_b a\beta \rangle + c_{21}^{ab} |2_a 1_b a\beta \rangle + c_{12}^{ab} |1_a 2_b a\beta \rangle + c_{22}^{ab} |2_a 1_b a\beta \rangle \]
\[ + c_1^{ab} |1 a_2 a_2 a\beta a\beta a\beta - 2(a\beta a\beta + a\beta a\beta)\rangle + c_2^{ab} |1 a_2 a_2 a\beta a\beta a\beta - 2(a\beta a\beta + a\beta a\beta)\rangle. \] (30)

Since there are 12 coefficients and 6 constraints, we expect to need 6 parameters except for additional possible phase factors.

The conditions from the (spin-integrated) occupation numbers are
\[ n_1^a = 2(|c_{11}^{ab}|^2 + |c_{21}^{ab}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + 6|c_1^{mm}|^2 + 2|c_2^{mm}|^2), \] (31a)
\[ n_2^a = 2(|c_{11}^{ab}|^2 + |c_{21}^{ab}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + 6|c_1^{mm}|^2 + 2|c_2^{mm}|^2), \] (31b)
\[ n_1^b = 2(|c_{11}^{ab}|^2 + |c_{21}^{ab}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + 6|c_1^{mm}|^2 + 2|c_2^{mm}|^2), \] (31c)
\[ n_2^b = 2(|c_{11}^{ab}|^2 + |c_{21}^{ab}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + |c_{12}^{ab}|^2 + |c_{22}^{bb}|^2 + 6|c_1^{mm}|^2 + 2|c_2^{mm}|^2). \] (31d)

Taking the difference between the occupation numbers in each irrep yields
\[ n_1^a - n_2^a = 2(|c_{11}^{ab}|^2 + |c_{12}^{ab}|^2 - |c_{21}^{ab}|^2 - |c_{22}^{ab}|^2 + 2(|c_1^{mm}|^2 - |c_2^{mm}|^2)), \] (32a)
As parameters we choose the following quantities

Assuming \(c_{i1}^{ab}, c_{i1}^{ab}, c_{i2}^{ab}\) and \(c_{i2}^{ab}\) to be given, \(|c_i|^2 - |c_{i2}|^2\) and \(|c_i|^2 - |c_{i2}|^2\) can be calculated.

There is one more non-trivial condition (i.e. apart from the trivial normalisation constraint)

Given \(c_{ij}^{ab} + c_{ij}^{bb}, \) we can obtain \(c_{ij}^{ab} - c_{ij}^{bb}\) or vice versa.

Now let us consider the two diagonality conditions (from the \(a_1\) and \(b_1\) irrep respectively)

Multiplying these equations by \(c_{i1}^{ab} + c_{i2}^{ab}\) and \(c_{i1}^{ab} + c_{i2}^{ab}\) respectively and subtracting them to eliminate \(c_{i1}^{ab}\) yields

Now writing everything in terms of \(c_{i1}^{ab}\) and \(c_{i2}^{ab}\)

we obtain

which can be rearranged as

Since \(|c_i|^2 - |c_{i2}|^2\) and \(|c_i|^2 - |c_{i2}|^2\) are known from (32a) and (32b) respectively, we have an equation for \((c_{i1}^{ab} + c_{i2}^{ab})^2 - (c_{i1}^{ab} + c_{i2}^{ab})^2\)

We have now all the ingredients for a parametrisation. As parameters we choose the following quantities

In a first step we can calculate the following intermediates

VI. CONCLUSION

It has been argued that the remaining degrees of freedom in the constrained search (6) are responsible for the possibility that identical occupation numbers can correspond to different 2RDMs. Different NOs lead to different two-electron integrals, which lead to a different minimum within the constrained-search functional (5) and hence, to different 2RDM matrix elements.

Symmetry is completely irrelevant for this feature. The proposal by Gritsenko to decompose the constrained-search functional as a minimisation over symmetry groups is not helpful, since the "no-symmetry" part already contains all other symmetry groups and is simple
identical the original exact functional. The exact functional can therefore not be regarded to be symmetry dependent.

It is however possible to put symmetry constraints on the exact functional. Though such a symmetry-restricted functional is only exact for systems with that symmetry, the advantage is that the variational freedom in the constrained search is reduced. This allows one to extract expressions from these symmetry-constrained functionals with less implicit parameters, which can serve as a guide in the construction of more general approximate 1RDM functionals. In this work, parametrisations for two symmetry-constrained functionals have been constructed which are exact for both the square \( H_2 \) and \( H_2+2H \) systems introduced by Wang and Knowles [1], as desired in Ref. [6]. These explicit expressions show that using only symmetry, not all variational freedom in the constrained-search functional can be eliminated, even for the \( H_2+2H \) system as claimed in [6]. Only if we also use that the two hydrogen atoms in the \( H_2+2H \) system are infinitely far away, we can perform the minimisation over the remaining additional parameters of the symmetry-restricted functional and obtain the 2RDM elements as an explicit expression in terms of the occupation numbers.

One can wonder whether we should invest in building approximate symmetry-restricted 1RDM functionals. Especially in light of the fact that explicit symmetry dependence reduces the validity of the functional to only a symmetry class of potentials / systems. Moreover, since 1RDM functional theory actually aims to be practical for medium sized systems which often do not display any symmetry, a 1RDM functional relying on symmetry would be of limited use. The only exception would be the spin states, since usually our molecular Hamiltonian is spin-independent. Being able to access the different spin states would actually be very useful in the description of transition-metal compounds.

Still it is worthwhile to search for possibilities to reduce the validity of the functional, because — inherited from the many-body wavefunction / density-matrix operator — the exact functional contains an exponentially growing amount of parameters \( \xi \). This makes an explicit construction of the functional infeasible and even undesirable for a practical purposes. By reducing the amount of potentials for which the functional needs to be valid, the flexibility of the wavefunction / density-matrix operator in the constrained-search functional can be reduced, so less parameters \( \xi \) need to be included in the functional. A viable alternative to reduce the validity of the functional is to exploit that we are typically only interested in a very limited class of external potentials, e.g. Coulomb potentials.

Nonetheless, the examples by Wang and Knowles [1] indicate that it might be unwise to aim for complete elimination of the parameters \( \xi \) to obtain an explicit functional for the 2RDM \( \langle i,j|k|\rangle = \Gamma_{i,j,k}(\mathbf{n}) \). The examples indicate that we need some degree of flexibility to accurately model ring-opening reactions. We also know that the flexibility in the signs in the two-electron functional (8) is important to describe the transition from the covalent to Van der Waals binding in \( H_2 \) [27, 28, 30]. Approximate functionals retaining some of the parameters \( \xi \) have actually already been developed [31–38] and future development of approximate functionals should be pursued in this direction.

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**Appendix A: 2RDM of the \( ^1B_{1g} \) state**

The 2RDM of the \( ^1B_{1g} \) state under the assumption \( n_{1a} \neq n_{2a} \). Due to the symmetry, the 2RDM becomes symmetry blocked. Abbreviating the orbitals as \( 1_a = 1a_g, 2_a = 2a_g, 1_b = 2b_a \) and \( 2_b = 3b_a \) the like-spin blocks become

\[
A_{ij}^{11} = \begin{pmatrix}
1_{1a},1_{1a} & 1_{1a},1_{2a} & 2_{1a},1_{1a} & 2_{1a},2_{1a} & 1_{2a},1_{1a} & 2_{2a},2_{1a}
\end{pmatrix}
\]

\[
A_{11}^{ij} = \begin{pmatrix}
2c_1^2 & 0 & 0 & 2c_1c_2 & 0 & 0
\end{pmatrix}
\]

\[
A_{12}^{ij} = \begin{pmatrix}
0 & 2c_1 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

\[
B_{ij}^{11} = \begin{pmatrix}
1_{1a},1_{1b} & 1_{1a},1_{2b} & 2_{1a},1_{1b} & 2_{1a},2_{1b} & 1_{2a},1_{1b} & 2_{2a},2_{1b}
\end{pmatrix}
\]

\[
B_{11}^{ij} = \begin{pmatrix}
d + 2e & d - 2e & 0 & 0 & 0 & 0
\end{pmatrix}
\]

\[
B_{12}^{ij} = \begin{pmatrix}
a & -h & 4e & -2h & 0 & 0
\end{pmatrix}
\]

\[
B_{21}^{ij} = \begin{pmatrix}
a & -h & 4e & -2h & 0 & 0
\end{pmatrix}
\]

\[
B_{22}^{ij} = \begin{pmatrix}
a & -h & 4e & -2h & 0 & 0
\end{pmatrix}
\]
where $a = c_1^2 + 5c_2^2$, $b = c_3^2 + 5c_3^2$, $d = c_1^2 + c_2^2$, $e = c_3^2$ and $h = c_3(c_2 - c_1)$.

### Appendix B: 2RDM of the $^1A_g$ state

Abbreviating the orbitals as $1_a = 1a_g$, $2_a = 2a_g$, $1_b = b_{2u}$, and $2_b = b_{3u}$ the like-spin blocks become. The 2RDM of the $^1A_g$ state becomes

\[
A^v_{ij} = 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a,
\]

where

\[
s_{ij} = |c^{ab}_{ij}|^2 + |c^{bb}_{ij}|^2, \quad t_j = c^{bb}_{ij}(c^{ab}_{ij} + c^{bb}_{ij}).
\]

The opposite-spin blocks become

\[
B^v_{ij} = 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a,
\]

where

\[
d^{a}_{i} = |c^{a}_{i2}|^2 + |c^{a}_{i1}|^2 + |c^{ab}_{i2}|^2, \quad (B7a)
\]

\[
d^{a}_{m} = |c^{a}_{i2}|^2 + |c^{a}_{m1}|^2 + |c^{ab}_{i2}|^2, \quad (B7b)
\]

\[
d^{b}_{i} = |c^{b}_{i2}|^2 + |c^{a}_{i1}|^2 + |c^{bb}_{i2}|^2 + 2|c^{b}_{i2}|^2, \quad (B7c)
\]

\[
p_{i} = c^{ab}_{i1}c^{a}_{i1} + c^{bb}_{i2}c^{b}_{i2}, \quad (B7d)
\]

\[
k_{i} = c^{ab}_{i1}c^{b}_{i1} - c^{ab}_{i2}c^{a}_{i2}, \quad (B7e)
\]

\[
l_{ij} = (c^{ab}_{i1}c^{a}_{i1} + c^{bb}_{i2}c^{b}_{i2})(c^{ab}_{j1}c^{a}_{j1} + c^{bb}_{j2}c^{b}_{j2}), \quad (B7f)
\]

\[
m = c^{ab}_{i1}c^{b}_{i1} + c^{ab}_{i2}c^{a}_{i2}, \quad (B7g)
\]

\[
n = |c^{a}_{i1}|^2 + |c^{b}_{i2}|^2, \quad (B7h)
\]

\[
q = c^{ab}_{i1}c^{ab}_{i2} + c^{ab}_{i1}c^{bb}_{i2} + c^{bb}_{i1}c^{b}_{i2} \quad (B7i)
\]

The other blocks are

\[
B^{v}_{ij} = 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a, \quad 1_a2_a,
\]

where $s_{ij}$ and $t_i$ were defined in (B5).

### Appendix C: Explicit minimisation for the $H_2 + 2H$ system

The advantage of this system is that most two-electron integrals are zero due to the distances. The only non-vanishing two-electron integrals are

\[
\begin{align*}
(1_a1_a|1_a1_a), & \quad (1_a1_b|1_a1_b), \\
(1_a1_b|1_b1_b), & \quad (1_b1_b|1_b1_b), \\
(2_a2_a|2_a2_a) &= \langle 2_a2_a|2_a2_a \rangle = w_H \\
(2_a2_b|2_a2_b) &= \langle 2_a2_b|2_a2_b \rangle = w_H
\end{align*}
\]

(C1)

This means that all blocks with $1_x2_y$ pairs $\{x,y \in \{a,b\}$ do not contribute and the interaction energy expression becomes

\[
W = s_{11}\left(3\langle 1_a1_b|1_a1_b \rangle - \langle 1_a1_b|1_b1_b \rangle \right) + \\
d_{11}^{a}\langle 1_a1_a|1_a1_a \rangle + \frac{1}{2}d_{12}^{ab}\langle 1_a1_b|1_b1_a \rangle + 2d_{12}^{bb}\langle 1_a1_b|1_b1_a \rangle + \\
\left(d_{22}^{a} + 2l_{22} + \frac{1}{2}d_{2b}^{b} + 2s_{2b} \right)w_H. \quad (C2)
\]

All terms only contain squares of the coefficients, so are always positive, except the $l_{ii}$ terms which read

\[
l_{11} = c_{21}^{ab}c_{11}^{aa} + c_{12}^{ab}c_{12}^{bb}, \quad l_{22} = c_{12}^{ab}c_{12}^{aa} + c_{21}^{bb}c_{12}^{bb}. \quad (C3)
\]

So if we choose

\[
c_{12}^{aa} > 0 \Rightarrow c_{12}^{bb} < 0, c_{21}^{ab} < 0, c_{12}^{bb} > 0, \quad (C4)
\]

we minimise the interaction energy. Now it is useful to write out the positively contributing terms explicitly

\[
W = (|c_{12}^{ab}|^2 + |c_{12}^{bb}|^2)(3\langle 1_a1_b|1_a1_b \rangle - \langle 1_a1_b|1_b1_b \rangle) + \\
( |c_{12}^{aa}|^2 + |c_{11}^{ab}|^2 + |c_{12}^{bb}|^2)(\langle 1_a1_b|1_a1_a \rangle + \\
\frac{1}{2}d_{12}^{ab}\langle 1_a1_b|1_b1_a \rangle + 2d_{12}^{bb}\langle 1_a1_b|1_b1_a \rangle + \\
( |c_{12}^{ab}|^2 + |c_{21}^{bb}|^2 + 3|c_{12}^{ab}|^2 + \\
2|c_{12}^{bb}|^2 + 2l_{22} + \frac{1}{2}d_{2b}^{b} + 2s_{2b} \rangle w_H. \quad (C5)
\]
We can minimise this expression if we can minimise $|c_{11}^{a}|^2$, $|c_{22}^{b}|^2$, $|c_{1}|^2$ and $|c_{2}|^2$, since they dominate over $|c_{11}^{a}|^2$, $|c_{22}^{b}|^2$, $|c_{11}^{a}|^2$ and $|c_{22}^{b}|^2$ terms because the latter also make negative contributions. The difference $|c_{11}^{a}|^2 - |c_{22}^{b}|^2$ is fixed by the occupation numbers (26c), so the best we can do is

$$c_{12}^{a} = \sqrt{\max(0, \Delta_0)}, \quad (C6a)$$

$$c_{12}^{b} = \sqrt{\max(0, -\Delta_0)}, \quad (C6b)$$

where $\Delta_0$ was defined in (27). Note that the phase of these coefficients does not matter, since they do not appear in any cross term in the interaction energy expression.

Now the parametrisation becomes very useful, since now we can vary over $\xi_1$, $\xi_2$ and $\xi_3$ without worrying about the constraints. Setting $\xi_3 = 0$, implies that $\xi_4 = 0$ (26a), so we can even achieve $|\xi_4|^2 = |\xi_2|^2 = 0$. The expression for the interaction then reduces to

$$W = |c_{11}^{a}|^2 (3(1_{a}1_{b}1_{a}1_{b}) - \langle 1_{a}1_{b}1_{a}1_{b} \rangle) + \frac{2}{3} n_{a}(1_{a}1_{b}1_{a}1_{b}) + \frac{1}{3} n_{b}(1_{a}1_{b}1_{a}1_{b}) + (2|c_{22}^{b}|^2 + \frac{1}{2} (n_{2a} + n_{2b})) w_H + 2\{1_{11}(1_{a}1_{b}1_{a}1_{b}) + 2\langle 1_{a}1_{b}1_{a}1_{b} \rangle \} w_H. \quad (C7)$$

All terms on the first three lines are now fixed and only the last line needs to be minimised. The last line can be rewritten as

$$W(\xi_1, \xi_2) = \xi_1 \xi_2 w_+ + \frac{\Delta_+ \Delta_-}{\xi_1} w_- \xi_2, \quad (C8)$$

where $w_\pm = w_H \pm \langle 1_{a}1_{b}1_{a}1_{b} \rangle$ and $2w_H \geq w_+ \geq w_- \geq 0$. The remaining variables are constrained by the normalisation (26d) as

$$\frac{1}{2} \left( \xi_1^2 + \frac{\Delta_+^2}{\xi_1} + \xi_2^2 + \frac{\Delta_-^2}{\xi_2} \right) = 1 - |\Delta_0|. \quad (C9)$$

We can solve this equation to get an expression for $\xi_1$ in terms of $\xi_2$. Due to the phase convention (C4), we should choose the positive root and since $w_+ > w_-$, we should choose the highest root for $\xi_1$, i.e.

$$\xi_1 = \frac{-1}{2\xi_2} \left[ 2(1 - |\Delta_0|) \xi_2^2 - \xi_2^2 - \Delta_-^2 + \sqrt{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^2 - \Delta_-^2} \right]^{1/2}. \quad (C10)$$

Now we insert this expression for $\xi_1$ back into (C8) and find its stationary points

$$0 = \frac{dW}{d\xi_2} = \frac{d\tilde{W}}{d[\xi]^{1/2} \frac{d[\xi_2]}{d\xi_2}}, \quad (C11)$$

where $[\cdot]$ is the part in square brackets in (C10). Since the solution $\xi_2 = 0$ is not suitable, one of the other derivatives needs to vanish. Let us first consider vanishing of the first derivative on the r.h.s.

$$0 = \frac{d\tilde{W}}{d[\xi]^{1/2} \frac{d\xi_2}{d\xi_2}} = -\frac{1}{2\xi_2} \left[ w_+ - \frac{2\Delta_+ \Delta_- w_-}{|\xi|} \right]. \quad (C12)$$

This equation is effectively a quadratic equation in $\xi_2^2$, so can be solved to yield

$$\xi_2^2 = \left( \frac{\Delta_+ w_+ + 1}{\Delta_- + w_-} \right) \left[ 1 - |\Delta_0| \right] \pm \sqrt{(1 - |\Delta_0|)^2 - (\Delta_+ w_+ - \Delta_-)(\Delta_+ w_+ + \Delta_-)}, \quad (C13)$$

where we should choose the largest root, since the first term in (C8) is dominant.

The other option is that the middle derivative on the r.h.s. of (C10) vanishes, $d[\xi]^{1/2}/d\xi_2 = 0$, which yields

$$0 = \frac{d[\xi]^{1/2}}{d\xi_2} = \frac{1}{[\xi]^{1/2}} \left( 1 - |\Delta_0| - \xi_2^2 \right) + \frac{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^4 - \Delta_+^2 \xi_2^2 - 2\Delta_+^2 \xi_2^2}{\sqrt{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^2 - \Delta_+^2 \xi_2^2 - 4\Delta_+^2 \xi_2^2}}. \quad (C14)$$

This is again effectively a quadratic equation in $\xi_2^2$, which can be solved to yield

$$\xi_2^2 = \frac{1}{2(1 - |\Delta_0|)} \left[ (1 - |\Delta_0|)^2 + \Delta_+^2 - \xi_2^4 \right] \pm \frac{\sqrt{(1 - |\Delta_0|)^2 + \Delta_+^2 - \xi_2^4} - \Delta_+^2 \xi_2^2}{\sqrt{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^2 - \Delta_+^2 \xi_2^2 - 4\Delta_+^2 \xi_2^2}}. \quad (C15)$$

We should again choose the largest root, which in this case is the one with the + sign, because $1 - |\Delta_0| \geq 0$.

The question is now which solution yields the global minimum? In the case of the $H_2 + 2H$, we know that the ground state 1RDM has $n_{2a} = n_{2b} = 1$, so $\Delta_+ = 0$ and $-1/2 \leq \Delta_0 = \Delta_- \leq 1/2$. This greatly simplifies the problem, since $\xi$ is now directly related by the constraint (C9) to $\xi_2$ as

$$\xi_1 = \frac{-1}{\xi_2} \sqrt{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^4 - \Delta_0^2} \quad (C16)$$

and the last line of the interaction energy (C8) reduces to

$$\tilde{W} = \xi_1 \xi_2 w_+ \quad (C17)$$

$$= -w_+ \sqrt{2(1 - |\Delta_0|) \xi_2^2 - \xi_2^4 - \Delta_0^2}. \quad (C18)$$

The only stationary point which converges to this point is (C15) with the plus sign, so we can hope that this point
always yields the minimum. This suspicion has been confirmed by a numerical check with Mathematica where the parameters are constrained as

\[ 0 \leq \frac{n_{-a}}{n_{+}} \leq 1, \]  
\[ -1 \leq \Delta_+ \leq 1, \]  
\[ 0 \leq |\Delta_0| \leq 1, \]  
\[ |\Delta_0| + |\Delta_-| + |\Delta_+| \leq 1, \]

where the latter condition is a result of working out

\[ \Delta_0 + \Delta_+ + \Delta_- = n_{1a} - 1, \]  
\[ \Delta_0 + \Delta_+ - \Delta_- = 1 - n_{2b}, \]  
\[ \Delta_0 - \Delta_+ + \Delta_- = 1 - n_{1b}, \]  
\[ \Delta_0 - \Delta_+ - \Delta_- = n_{2a} - 1. \]

By putting the most extreme occupation numbers (0 or 2) we find that all left-hand sides \( \in [-1, 1] \), so (C19d) follows.

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