Time evolution of fermionic occupation numbers

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By employing the recently generalized Pauli exclusion principle, we derive an equation for the time evolution of the natural occupation numbers for fermionic systems. The evolution of such numbers is related with the evolution of the natural orbitals and a set of many-body relative phases. We then relate the evolution of these phases to a dynamical, a geometrical, and a correlated term, attached to each one of the Slater determinants appearing in the configuration-interaction expansion of the wave function. This time-evolution of the phases is absent in current electronics theories based on reduced density matrices, which explains their severe shortcomings in dealing with time-dependent fermionic occupations. We then exemplify the quality of our approach by comparing the predictions of our theory for a out-of-equilibrium three-electron Hubbard model. Finally, we give a few hints on how to generalize our results to systems with more than three active electrons.

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The time evolution of an electronic system is governed by the Schrödinger equation \cite{1}. Yet a real-time propagation of the many-fermion wave function is, by and large, computationally prohibitive. The time-dependent extension of density functional theory (DFT) alleviates this computational problem by mapping the evolution of the ground-state density to the one of a certain auxiliary system \cite{2}. Since such auxiliary system is non-interacting, time dependent DFT does not involve fractional occupation numbers, which are at any rate important for capturing quantum correlations \cite{3}, even in the adiabatic regime \cite{4}.

Reduced density matrix functional theory (RDMFT) is based on a theorem \cite{5} asserting that the ground-state wave function can be written as a functional of the one-body reduced density matrix:

$$\gamma(1,1') \equiv \langle \Psi_{\text{gs}} | \psi(1') \psi(1) | \Psi_{\text{gs}} \rangle,$$

with the short notation $1 \equiv (r_1, s_1)$ for position and spin coordinates. Thus, ground states can be viewed as functionals of such reduced densities (say, $\Psi_{\text{gs}}[\gamma]$). Since RDMFT accounts for fractional natural occupation numbers (i.e., the eigenvalues of $\gamma$), it captures quite well strong (static) electron correlations \cite{6–9}. For instance, unlike DFT, RDMFT correctly predicts the insulating behavior of Mott-type insulators \cite{10, 11}. Furthermore, it has been recently pointed out that $\gamma$ encodes essential many-body aspects of interacting fermions and hard-core bosons, as many-body localization transitions \cite{12, 13}, entanglement \cite{14}, or topological states \cite{15}. Given these remarkable properties, there is a growing interest in proposing protocols to access to the structure of this density matrix both experimentally using quantum-gas microscopes \cite{16}, or theoretically employing quantum computers \cite{17}.

Unfortunately, time-dependent extensions of RDMFT suffer from various shortcomings. Chief among them, the current status of the theory does not allow the fermionic occupation numbers to evolve in time \cite{18–23}. It is known that this deficiency is connected to the failure of RDMFT to account for relative phases at the level of the two-body reduced density matrix \cite{4, 24, 25}. Based on recent progress on our understanding of fermionic exchange symmetry \cite{26–30}, this paper is aimed at proposing a new way of tackling the time dependency of the natural occupation numbers of fermionic systems.

From a formal viewpoint, it is known that the compatibility, or representability, of a fermionic one-body reduced density matrix $\gamma$ with respect to a quantum many-body state $|\Psi\rangle$ is described by sets of linear constraints on its spectra $n \equiv (n_1, n_2, \ldots)$, namely \cite{31}:

$$\mathcal{D}_j(n) \equiv \kappa_j^0 + \sum_i \kappa_j^i n_i \geq 0,$$

where the coefficients $\kappa_j^i$ are integers. Along with the non-increasing ordering of the natural occupation numbers (say, $n_i \geq n_{i+1}$) and the sum rule ($\sum_i n_i = N$), these generalized Pauli constraints \eqref{eq:2} define a polytope where the sets of $n$, which are compatible with $N$-fermion pure states, lie. It is quite remarkable that whenever some of those quantum marginal constraints are saturated or pinned the total quantum state has a specific, simplified structure. Indeed,

$$\mathcal{D}_j(n) = 0 \iff \hat{D}_j |\Psi\rangle = 0,$$

where the operator $\hat{D}_j \equiv \mathcal{D}_j(\hat{n}) = \kappa_j^0 + \sum_j \kappa_j^i \hat{n}_i$ is built by replacing the occupation numbers in Eq. \eqref{eq:2} by the corresponding particle number operators.

The importance of the result \eqref{eq:3} lies on the fact that it not only connects the $N$- and the 1-particle pictures, which is in itself striking, but also provides an important selection rule for the Slater determinants that can appear in the configuration-interaction expansion of pinned wave functions \cite{27}. Indeed, a wave function whose spectrum is

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pinned to one of the polytope’s facets $\mathcal{P}_j = \{ \mathbf{n} | D_j(\mathbf{n}) = 0 \}$ can be written as a linear superposition of the Slater determinants which belong to the zero-eigenspace of the operator $D_j$. This selection rule can be used to systematically produce Ansätze for ground states in the form of sparse wave functions, which, instead of using the full Hilbert space, can be expanded in the basis of the natural orbitals (the eigenvalues of $H$) with a few Slater determinants [27, 32]. Apart from the simplification of the wave function, there is another advantage in using natural orbitals that is worth mentioning here: it is known that the basis of natural orbitals is the optimal basis to approximate the full wave function by a finite basis of one-particle functions, giving therefore a superior convergence [33].

Remarkably, the structural simplification for pinned quantum systems (3) is stable in the sense that any many-fermion quantum state $|\Phi\rangle$ can be approximated by the structural simplified form corresponding to saturation of the generalized Pauli constraint $D_j$. The error of such a simplification is bounded by twice the distance of the vector of its occupation numbers $\mathbf{n}_\Phi$ to the corresponding polytope’s facet $\mathcal{P}_j$ [28, 29]:

$$1 - ||\hat{P}_j\Phi||^2 \leq 2D_j(\mathbf{n}_\Phi),$$

where $\hat{P}_j$ is the projector on the zero-eigenspace of $\hat{D}_j$. Recently, we have used this stability result to propose new stastically correlated functionals within RDMFT with excellent results for electronic systems with an odd number of electrons [34]. It has also been suggested that the generalized Pauli constraints may facilitate the development of more accurate functionals [35]. In fact, the simplified structural form of pinned wave functions given by Eq. (3) allows one not only to efficiently approach to the wave function, but also, for some cases, to explicitly write the two-body reduced density matrix in terms of $\gamma$. Since quasipinning (say, $D_j(\mathbf{n}) \approx 0$) is approximately the case of several ground states, the quasipinning mechanics has attracted the attention of some theoreticians in quantum chemistry and quantum information [36–45].

We can also show that the structural simplification of the wave function (3) is also stable in the sense that pinning is robust under any small perturbation of the Hamiltonian. This is our first result. For the demonstration, let us assume that $|\Psi_0\rangle$ is the ground state of a system driven by the Hamiltonian $\hat{H}$ (whose non-degenerated eigenstates are $|\Psi_n\rangle$ with eigen-energies $E_n$). The distance to a given polytope’s facet can be written by means of the number operators, namely,

$$D_j(\mathbf{n}_0) = \kappa_j^0 + \sum_i \kappa_j^i |\Psi_0\rangle \hat{n}_i |\Psi_0\rangle.$$  

Assume also that $D_j(\mathbf{n}_0) = 0$ (i.e., the state is pinned to that boundary). In Rayleigh-Schrödinger perturbation theory the ground state of the perturbed Hamiltonian

$$\hat{H}(\lambda) \equiv \hat{H} + \lambda \hat{V}$$

reads $|\Psi_0^\lambda\rangle = |\Psi_0\rangle + \lambda \sum_n b_n |\Psi_n\rangle + \mathcal{O}(\lambda^2)$. The corresponding reduced density matrix is then

$$\hat{\gamma}_0^\lambda \equiv \text{Tr}_N \frac{\langle \Psi_0^\lambda \rangle |\Psi_0^\lambda\rangle}{|\Psi_0^\lambda\rangle} \approx \hat{\gamma}_0 + \lambda \sum_n b_n \text{Tr}_N \{ |\Psi_n\rangle \langle \Psi_0^\lambda \rangle \} + \mathcal{O}(\lambda^2).$$

Thus, as expected, the tangent space at $|\Psi_0\rangle$ maps to a tangent space at $\hat{\gamma}_0$. Notice that the distance to the polytope’s facet changes in the following way:

$$\frac{\partial D_j(\mathbf{n}^\lambda)}{\partial \lambda} \bigg|_{\lambda=0} = \sum_i \kappa_j^i |\varphi_i^\lambda\rangle \frac{\partial |\varphi_i^\lambda\rangle}{\partial \lambda} |\varphi_i^\lambda\rangle \bigg|_{\lambda=0} = \sum_i \kappa_j^i \sum_{n \neq 0} b_n \text{Tr}_N [\hat{n}_i |\Psi_n\rangle \langle \Psi_0^\lambda \rangle + \text{c.c.}] = 2 \sum_{n \neq 0} b_n \text{Re} \langle \Psi_n |\hat{D}_j |\Psi_0^\lambda\rangle = 0,$$

where $\kappa_j^\lambda$ are the eigenvalues and $|\varphi_i^\lambda\rangle$ the eigenfunctions of $\hat{\gamma}_0^\lambda$. In the second line of (8) we have used the formula for the first-order correction according to Rayleigh-Schrödinger perturbation theory. In the last line we have used the fact that the wave function $|\Psi_0\rangle$ is an eigenfunction of $\hat{D}_j$. Therefore, for pinned systems, in leading order, $D_j(\mathbf{n}^\lambda) \approx D_j(\mathbf{n}_0) = 0$. The moral is that, under any small perturbation, a pinned system remains pinned to the polytope’s boundary. For a quasipinned system (i.e. $D_j(\mathbf{n}^\lambda) \approx 0$), this also holds approximately.

This robustness of (quasi)pinning prompts us to seek for the equation of motion of the one-body reduced density matrix of a pinned quantum system. Geometrically, the aim is to constrain the dynamics of the system to move on a hyperplane in the one-particle picture. The Schrödinger equation leads to the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy, whose equation for $\gamma(t)$ is [46]:

$$i\hbar \partial_t \gamma(t) = [\hat{h}(t), \gamma(t)] + \hat{u}(t),$$

where $\hat{h}(t)$ is the time-dependent one-particle Hamiltonian operator, $\hat{u}(t)$ is (in spatial and spin representation)

$$u(1, 1', t) = 2 \int \{ v(1, 2) - v(1', 2) \} \Gamma(1, 2; 1', 2, t) d2,$$

and $v(1, 2)$ is the Coulomb potential. As usual, the two-particle reduced density matrix can be computed by means of the field operators, namely, $\Gamma(1, 2; 1', 2, t) \equiv \frac{1}{2} \langle \hat{\Psi}(t) |\hat{\psi}^\dagger(1') \hat{\psi}^\dagger(2) \hat{\psi}(2) \hat{\psi}(1) |\Psi(t)\rangle$. Notice that the density matrix $\hat{\gamma}(t)$ can also be computed by integrating out $\Gamma(t)$ which satisfies in turn an equation similar to (9). However, this latter procedure is incorrect for it is not energy conserving. For this reason, fermionic constraints on the occupation numbers should play a role in implementing the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy [47].
Recall that, in the natural-orbital basis, $\dot{\gamma}(t)$ is diagonal, reading $\dot{\gamma}(t) = \sum_k n_k(t) \langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle$. Multiplying Eq. (9) by $\varphi_j^* (1) \varphi_j (1')$, and integrating both position and spin coordinates we obtain:

$$i\hbar [\hat{n}_{jk} + n_j \langle \varphi_j | \dot{\varphi}_k \rangle + n_k \langle \varphi_j | \dot{\varphi}_k \rangle] = (n_k - n_j) \langle \varphi_j | \dot{\varphi}_k \rangle + W_{jk} - W_{kj}^*, \quad (10)$$

where $W_{jk} = \sum \Gamma_{1j} \Gamma_{1'k} d_1 d_{1'} d_2$ is a further contraction of the two-body density matrix. The non-diagonal terms of Eq. (10) give the time-evolution for the natural orbitals: for $j \neq k$ we obtain

$$i\hbar \langle \varphi_j | \dot{\varphi}_k \rangle = (n_k - n_j) \langle \varphi_j | \dot{\varphi}_k \rangle + W_{jk} - W_{kj}^* \frac{n_k - n_j}{n_k - n_j}. \quad (11)$$

Taking $j = k$ in Eq. (10) we obtain an equation for the time evolution of the natural occupation numbers:

$$\dot{n}_k = \frac{2}{\hbar} \Im [W_{kk}]. \quad (12)$$

Since the imaginary part of $W_{kk}$ determines the time evolution of the occupations, it is clear that the relative phases are crucial to correctly capture the dynamics of the system. The current ground-state reconstructions in RDMFT are very restrictive, for they only contain the so-called two-index (direct and exchange) Coulomb integrals. With the exception of the Löwdin-Shell functional for two-electron systems [48], the right-hand of (12) vanishes identically, so the occupation numbers do not evolve in time [49]. This imposes a serious disadvantage and explains why the time-dependent extension of RDMFT is so challenging. To shed light into this problem we study the evolution of the one-body reduced density matrix for pinned wave functions, which, as we have shown, are structural simplifications of some ground states.

To illustrate our approach let us consider the so-called Borland-Dennis wave function, namely, the pinned rank-six approximation (i.e., six modes or six natural spin-orbitals) for the three-active-electron system [50]. This wave function is known to be pinned to one of the facets of the polytope (i.e., $n_1 + n_2 + n_4 = 2$) and can be written explicitly in terms of the natural occupation numbers $n$, the natural orbitals $\varphi$ and the relative phases $\xi$. It reads:

$$| \Phi_{BD}(n, \varphi, \xi) \rangle = \sum_{\alpha} \sqrt{n_{\alpha}} e^{-i\xi_{\alpha} / \hbar} | \varphi_{\alpha} \rangle, \quad (13)$$

where $\{ \cdot \}$ denotes a normalized Slater determinant. From now on, Greek letters stand for $\{ 3, 5, 6 \}$, and $\varphi_3(t) \equiv \varphi_1(t) \varphi_2(t) \varphi_3(t), \varphi_5(t) \equiv \varphi_1(t) \varphi_4(t) \varphi_5(t)$ and $\varphi_6(t) \equiv \varphi_2(t) \varphi_4(t) \varphi_6(t)$. Without loss of generality, the relative phases $\xi_\alpha$ and the natural orbitals are taken real. For the wave function (13) there are four saturated generalized Pauli constraints, namely, $n_k + n_{7-k} = 1$, and $n_1 + n_2 + n_4 = 2$ (or, equivalently, $n_3 + n_5 + n_6 = 1$).

In the Appendix we show that, for the Borland-Dennis wave function, we have $W_{kk} - W_{kk}^* \neq 0$ for all $k$, and therefore we obtain an explicit equation for the evolution of the natural occupation numbers

$$\dot{n}_\alpha = \frac{i}{\hbar} \sum_{\beta \neq \alpha} \frac{\sqrt{n_{\alpha} n_{\beta}}}{\sqrt{n_{\alpha} n_{\beta}}} \left( \langle \varphi_{\alpha} | \hat{H} | \varphi_{\beta} \rangle e^{i(\xi_\alpha - \xi_\beta)} - c.c. \right), \quad (14)$$

where $\alpha, \beta \in \{ 3, 5, 6 \}$. Eq. (14) is the second result of this paper. By restricting the evolution to one of the hyperplanes in the one-particle picture, coming from the representability conditions, we are able to unveil an equation for the evolution of the occupation numbers of a three-active electron system, and give an explicit expression. Notice in passing that $\sum_\alpha \dot{n}_\alpha = 0$, as it should be. Notice also that the evolution of the fermionic occupation numbers in Eq. (14) is mediated by the two-particle interaction only.

To complete the time-evolution picture of the quantum-mechanical system we need equations for the evolution of the relative phases $\xi$. The evolution of the natural orbitals is given by the equation (11), plus the fact that $\langle \varphi_k | \dot{\varphi}_k \rangle = 0$. On the other hand, the dynamical equations for $\xi$ can be derived from the stationary condition of the action $A(\Phi_{BD}) = \int_0^\tau (\Phi_{BD}(\tau)) d\tau - \hat{H}(\tau)|\Phi_{BD}(\tau)\rangle d\tau$ with respect to the fermionic occupation numbers. In the Appendix we show that the evolution of the relative phases is determined by a quite simple equation, namely,

$$\dot{\xi}_\alpha = \langle \varphi_{\alpha} | \hat{H}(t) - i\hbar \partial_t | \varphi_{\alpha} \rangle + \phi^{corr}_{\alpha}. \quad (15)$$

This result relates the evolution of the phases with (i) a Slater-dynamical phase $\phi^{dyn}_{\alpha}$ attached to the Slater determinant $| \varphi_{\alpha} \rangle$ (given by $\langle \varphi_{\alpha} | \hat{H}(t) | \varphi_{\alpha} \rangle$), (ii) a Slater-geometrical phase $\phi^{geo}_{\alpha} = -i\hbar \langle \varphi_{\alpha} | \partial_t | \varphi_{\alpha} \rangle$, and (iii) an additional correlated phase which is written in terms of the non-diagonal elements of the Hamiltonian, namely,

$$\phi^{corr}_{\alpha} = \frac{1}{2} \frac{1}{\sqrt{n_{\alpha}}} \sum_{\beta \neq \alpha} \sum_{\beta \neq \alpha} \sqrt{n_{\beta}} \left( \langle \varphi_{\alpha} | \hat{H} | \varphi_{\beta} \rangle e^{i(\xi_\alpha - \xi_\beta)} + c.c. \right).$$

Since the seminal paper of Berry [51], this kind of phases has been discovered in many fields of physics [52–55]. Therefore, it comes as no surprise that we encounter such phases here. Yet the result (15) is unique in establishing a direct relationship for fermionic systems between Slater determinants $| \varphi_{\alpha} \rangle$ and the phases $\xi_{\alpha}(t)$. Moreover, since the wave function and the Slater determinants are written in terms of the natural orbitals and the occupation numbers, the phases presented here are functions of one-body reduced quantities (say, $\phi^{dyn}_{\alpha} [\gamma]$, $\phi^{geo}_{\alpha} [\gamma]$ and $\phi^{corr}_{\alpha} [\gamma, \xi]$). We emphasize that Eq. (15) is absent from the standard formulation of time-dependent RDMFT, and this is the reason for its severe shortcomings.

Notice that the result (15) can be easily generalized to any natural orbital which appears in one and only one of the Slater determinants in the configuration-interaction expansion of the wave function. This latter observation
section we discuss the exact computation of the time-evolution of the natural occupation numbers. Indeed, we can take the orbitals appearing only once and associate the corresponding occupation numbers and the Slater-dynamical and Slater-geometrical phases. For time-independent Hamiltonians and for ground states, equations (14) and (15) predict correctly, as it should be, that \( \hat{n}_\alpha = 0 \).

We investigate the quality of our approach by studying the three-particle Hubbard model, whose Hamiltonian reads:

\[
\hat{H}(t) = -\tau \sum_{\langle i, j \rangle, \varsigma} c_{i\varsigma}^\dagger c_{j\varsigma}^\dagger + u \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow},
\]

where \( \langle i, j \rangle \) denotes nearest neighbor sites and \( \varsigma \in \{\uparrow, \downarrow\} \). As customary, we take from now on \( \tau = 1 \) as the unit of energy of the system. We furthermore look at the strongly correlated limit by choosing the parameters \( u = 2 \). The Hamiltonian as written in (16) is time-independent, therefore, to induce a time-dependence we shifted the ground-state occupations of the three states to \( n_1 \to n_1, n_2 \to n_2 - \delta, n_3 \to n_3 - \delta, n_4 \to n_4 + \delta, n_5 \to n_5 + \delta \) and \( n_6 \to n_6 \), with \( \delta = 0.02 \).

In Fig. 1 we compare the exact evolution for the system together with our RDMFT-based approach. The agreement between the time-evolution of the occupation numbers is perfectly described by Eq. (14) until around \( t = 7 \), from which a small dephasing is noticeable. The agreement remains nevertheless remarkable, especially when one considers that standard time-dependent RDMFT, with currently available functionals, would yield constant occupations.

In conclusion, we investigated the time evolution of the one-body reduced density matrix, by using the recently generalized Pauli principle for pure states. We presented three important results. First, we showed that the structural simplification of the wave function is stable under any small perturbation of the Hamiltonian. This result allows us to employ a simplified wave function during the time evolution of the system as an Ansatz to the full wave function. Second, we developed a closed expression for the time evolution of the fermionic natural occupation numbers. Finally, we have presented a formula for the evolution of the phases. Such phases can be identified by their dynamical, geometrical and correlated parts. We believe that this last equation is the missing piece for the successful application of reduced density-matrix functional theory to time-dependent problems. Since our approach is accurate and alleviates the computational burden of the many-body problem, we think that it can be an important tool to understand time-evolving fermionic systems, whose physics is receiving increased attention.

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Appendix A: Supplemental material

This supplemental material is divided in three parts. In the first one, we present the computation of the time evolution of the natural occupation numbers and the relative phases attached to each one of such numbers for the Borland-Dennis state. In the second we prove that \( \Im[W_{kk}] \neq 0 \) for the Borland-Dennis wave function. This result tells us that the time-evolution comes from the coherent-superposition structure of the wave function. In the last section we discuss the exact computation of the time-evolution of the natural occupation numbers.

1. Time evolution of the Borland-Dennis state

Consider a \( N \)-fermion time-dependent Hamiltonian given by

\[
\hat{H}(x_1, \ldots, x_N; t) = \sum_i \hat{h}(x_i; t) + \sum_{i<j} \hat{v}(x_i, x_j).
\]  

(\ref{eq:1})
Here \( \hat{h}(\mathbf{x}; t) \) stands for the time-dependent one-particle Hamiltonian and \( \hat{v}(\mathbf{x}, \mathbf{y}) \) is the two-particle interaction. Here we are interested in the time evolution of the three-electron Borland-Dennis state which reads:

\[
|\Phi_{\text{BD}}(t)\rangle = \sqrt{n_3(t)} e^{-i\xi_3(t)} |\varphi_1(t)\varphi_2(t)\varphi_3(t)\rangle + \sqrt{n_5(t)} e^{-i\xi_5(t)} |\varphi_1(t)\varphi_4(t)\varphi_5(t)\rangle + \sqrt{n_6(t)} e^{-i\xi_6(t)} |\varphi_2(t)\varphi_4(t)\varphi_6(t)\rangle \\
\equiv \sum_\alpha \sqrt{n_\alpha(t)} e^{-i\xi_\alpha(t)/\hbar} |\varphi_\alpha(t)\rangle,
\]

where \(|\cdot\rangle\) denotes a Slater determinant. In Eq. (A2) greek letters stand for \{3, 5, 6\} and \(\varphi_3(t) \equiv \varphi_1(t)\varphi_2(t)\varphi_3(t)\), \(\varphi_5(t) \equiv \varphi_1(t)\varphi_4(t)\varphi_5(t)\), and \(\varphi_6(t) \equiv \varphi_2(t)\varphi_4(t)\varphi_6(t)\). Just as in the Shull-Löwdin wave function for the two-electron case [48], the natural orbitals \(\{\varphi_k\}\), the natural occupation numbers \(\{n_k\}\) and the relative phases \(\{\xi_k\}\) appear explicitly in the wave function \(|\Phi_{\text{BD}}\rangle\).

The time derivative of the wave function (A2) is

\[
\dot{\Phi}_{\text{BD}} = \sum_\alpha \frac{i\hbar}{2} \left( \frac{\dot{n}_\alpha}{\sqrt{n_\alpha}} + \sqrt{n_\alpha} \dot{\xi}_\alpha \right) e^{-i\xi_\alpha/\hbar} |\varphi_\alpha\rangle + i\hbar \sum_\alpha \sqrt{n_\alpha} e^{-i\xi_\alpha/\hbar} \partial_t |\varphi_\alpha\rangle,
\]

and therefore the global geometric phase is:

\[
\langle \Phi_{\text{BD}} | i\hbar \partial_t | \Phi_{\text{BD}} \rangle = \sum_\alpha n_\alpha \dot{\xi}_\alpha + i\hbar \sum_\alpha n_\alpha \langle \varphi_\alpha | \partial_t | \varphi_\alpha \rangle.
\]

We have used the fact that \(\sum_\alpha \dot{n}_\alpha = 0\) and \(\langle \varphi_\beta | \partial_t | \varphi_\alpha \rangle = 0\), whenever \(\beta \neq \alpha\), because the Slater determinants in (A2) differ by more than two orbitals. The expected value of the Hamiltonian (A1) is:

\[
\langle \Phi_{\text{BD}} | \hat{H} | \Phi_{\text{BD}} \rangle = \sum_\alpha n_\alpha \langle \varphi_\alpha | \hat{H} | \varphi_\alpha \rangle + \sum_{\alpha \neq \beta} \sqrt{n_\alpha n_\beta} e^{i(\xi_\alpha - \xi_\beta)/\hbar} \langle \varphi_\beta | \hat{H} | \varphi_\alpha \rangle.
\]

The optimization of the action functional \(A[n, \varphi, \xi] = \int_0^1 \langle \Phi_{\text{BD}}(\tau) | i\hbar \partial_{\tau} - \hat{H}(\tau) | \Phi_{\text{BD}}(\tau) \rangle d\tau\), gives an equation for the evolution of the occupation numbers, namely,

\[
\dot{n}_\alpha = \frac{i}{\hbar} \sum_{\beta \neq \alpha} \sqrt{n_{\alpha} n_{\beta}} \left[ \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle e^{i(\xi_\alpha - \xi_\beta)/\hbar} + \text{c.c.} \right]
\]

and for the time evolution of the relative phases, namely,

\[
\dot{\xi}_\alpha = \langle \varphi_\alpha | \hat{H} - i\hbar \partial_t | \varphi_\alpha \rangle + \phi_\alpha^{\text{corr}},
\]

where \(\phi_\alpha^{\text{corr}} = \frac{1}{2\sqrt{n_\alpha}} \sum_{\beta \neq \alpha} \sqrt{n_\beta} \left[ \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle e^{i(\xi_\alpha - \xi_\beta) + \text{c.c.}} \right]\). Notice in passing that \(\sum_\alpha \dot{n}_\alpha = 0\).

For the particular case where the Hamiltonian is symmetric in the Slater determinants basis set \(\langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle = \langle \varphi_\beta | \hat{H} | \varphi_\alpha \rangle\) we obtain the closed formulae:

\[
\dot{n}_\alpha = -\frac{2}{\hbar} \sqrt{n_\alpha} \sum_{\beta \neq \alpha} \sqrt{n_\beta} \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle \sin \left[ (\xi_\alpha - \xi_\beta) / \hbar \right]
\]

and

\[
\dot{\xi}_\alpha = \langle \varphi_\alpha | \hat{H} - i\hbar \partial_t | \varphi_\alpha \rangle + \frac{1}{\sqrt{n_\alpha}} \sum_{\beta \neq \alpha} \sqrt{n_\beta} \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle \cos \left[ (\xi_\alpha - \xi_\beta) / \hbar \right].
\]

Finally, we can give a closed formula for the evolution of the natural occupation numbers:

\[
n_\alpha(t) = \left\{ \sqrt{n_\alpha(0)} - \hbar^{-1} \int_0^t \sum_{\beta \neq \alpha} \sqrt{n_\beta(\tau)} \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle \sin \left[ (\xi_\alpha - \xi_\beta) / \hbar \right] d\tau \right\}^2.
\]
2. $W_{kk} - W_{kk}^* \neq 0$ for the Borland-Dennis state

Recall that

$$W_{jk} \equiv 2 \int v(1, 2) \Gamma(1, 2; 1', 2) \varphi_j^*(1) \varphi_k(1')d1'd2.$$  \hspace{1cm} (A11)

This expression is equivalent to the two-particle energy expression $W = \int v(1, 2) \Gamma(1, 2; 1, 2)d1d2$ by replacing $\varphi_k^*(1)$ for $\varphi_j^*(1)$. Thus,

$$W_{kk} \equiv 2 \int v(1, 2) \Gamma(1, 2; 1', 2) \varphi_k^*(1) \varphi_k(1')d1'd2.$$  \hspace{1cm} (A12)

For the Borland-Dennis state

$$\hat{\Gamma}_{BD} = \sum_{\alpha\beta} \sqrt{n_\alpha n_\beta} e^{-i(\xi_\alpha - \xi_\beta)/\hbar} \int |\varphi_\alpha\rangle\langle\varphi_\beta|dx_3$$  \hspace{1cm} (A13)

and therefore it is easy to verify that

$$W_{33} = n_3 \langle \varphi_1 \varphi_3 | \hat{v} | \varphi_1 \varphi_3 \rangle + n_3 \langle \varphi_2 \varphi_3 | \hat{v} | \varphi_2 \varphi_3 \rangle + \sum_{\beta \neq 3} \sqrt{n_3 n_3} e^{i(\xi_3 - \xi_\beta)/\hbar} \langle \varphi_3 | \hat{v} | \varphi_\beta \rangle$$  \hspace{1cm} (A14)

and therefore $W_{33} - W_{33}^* = \sum_{\beta \neq 3} \sqrt{n_3 n_3} e^{i(\xi_3 - \xi_\beta)/\hbar} \langle \varphi_3 | \hat{v} | \varphi_\beta \rangle - c.c. \neq 0$. The same calculation leads to $W_{kk} - W_{kk}^* \neq 0$, $\forall k$. This result shows that the evolution of the occupation numbers comes from the coherent superposition of Slater determinants in the many-body wave function.

3. Exact evolution of the natural occupation numbers

Consider a general many-electron wave function written in a complete basis set of Slater determinants:

$$|\Phi(t)\rangle = \sum_\alpha c_\alpha(t)|\varphi_\alpha\rangle.$$  \hspace{1cm} (A15)

Alternatively, this wave function can be written in the eigenbasis of a given time-independent Hamiltonian,

$$|\Phi(t)\rangle = \sum_j d_j e^{-iE_jt/\hbar} |\psi_j\rangle.$$  \hspace{1cm} (A16)

Since each eigenvector can be written as a linear superposition of the Slater determinants (say, $|\psi_j\rangle = \sum_\alpha \Lambda_{\alpha j} |\varphi_\alpha\rangle$), Eqs. (A15) and (A16) can be compared. Therefore,

$$\sum_\alpha c_\alpha(t)|\varphi_\alpha\rangle = \sum_j d_j e^{-iE_jt/\hbar} \Lambda_{\alpha j} |\varphi_\alpha\rangle.$$  \hspace{1cm} (A17)

For the case of the Borland-Dennis wave function (A2) we have $n_\alpha(t) = |c_\alpha(t)|^2$. This procedure requires of course the exact diagonalization of the Hamiltonian in use, which, for all practical purposes, is a major drawback.

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