Generalized variational principle for the time-dependent Hartree-Fock equations for a Slater determinant

H.-J. Kull

Institut für Theoretische Physik A, Rheinisch Westfälische Technische Hochschule, D-52056 Aachen, Germany

D. Pfirsch

Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany

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The time-dependent Hartree-Fock equations are derived from a variational principle for the general N-body action of a Slater determinant of single-electron orbitals. The variational principle generalizes commonly used variational treatments based on reduced two-body actions. The self-consistent field equations are found to contain time-dependent corrections to the standard mean-field interactions. Their physical significance is discussed and a time-dependent phase shift to the Slater determinant is obtained that properly accounts for the total interaction energy in the mean-field approach.

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I. INTRODUCTION

The time-dependent Hartree-Fock (TDHF) method describes the time evolution of a many-body system by an approximate set of self-consistent mean-field equations for single-particle wave functions. In the past, the time-dependent generalization of the static Hartree-Fock (HF) theory has been of particular interest for dynamical studies of nuclear reactions [1], atomic collisions [2], and multiphoton ionization [3]. The calculation of single-particle TDHF wave functions also has greatly stimulated research on associated numerical techniques [4].

The TDHF approach commonly is based on a variational principle for the time-dependent Schrödinger equation along with an approximation of the many-body wave function by a Slater determinant of single-particle wave functions. For two-body interactions the action can be reduced to a two-body functional that provides the basis of previous variational approaches. A thorough discussion of this variational formulation has been given in Ref. [5], which appears to be the basis of many later applications of the method. A comprehensive derivation of the standard TDHF model used in atomic physics can be found in Ref. [6].

In the present work, we review and extend the variational formulation of the TDHF equations for a Slater determinant. In contrast to previous work, the action is not reduced to a two-body functional. Instead, the complete N-body action is minimized with respect to arbitrary variations of the single-electron wave functions. In the following, all equations are written in atomic units.

To illustrate the basic difference between these variational formulations, consider a single-electron Schrödinger equation

$$i\frac{\partial \psi}{\partial t} = [H_0 + V(t)]\psi \quad (1.1)$$

with a Hermitian Hamiltonian H_0 and an additional time-dependent interaction potential $V(t)$. This equation can simply be recovered from the variation of the action

$$S[\psi, \psi^*] = \int dt \int d^3r \, \psi^* \left(H_0 + V(t) - i\frac{\partial}{\partial t}\right)\psi \quad (1.2)$$

with respect to ψ^*. On the other hand, if the wave function is assumed normalized to unity, the reduced action becomes,

$$S'[\psi, \psi^*] = V(t) + \int dt \int d^3r \, \psi^*(H_0 - i\partial_t)\psi. \quad (1.3)$$

Variation of S' with respect to ψ^* yields again the Schrödinger equation (1.1), however, without the potential $V(t)$. This example clearly demonstrates that the variational forms S and S' are not equivalent. The above discrepancy can be removed by adding an orthonormality constraint to the action S'

$$S'' = S' + \int dt \, \mu(t) \int d^3r \, \psi^* \psi \quad (1.4)$$

with a Lagrange multiplier $\mu(t)$ at each time t. The variation of S'' now yields,

$$i\frac{\partial \psi}{\partial t} = [H_0 + \mu(t)]\psi. \quad (1.5)$$

To obtain the correct result $\mu(t) = V(t)$, the Lagrange multiplier has to be determined in accordance with the complete action by setting

$$S = S''. \quad (1.6)$$

From this example one can draw the following conclusions. Making use of the orthonormality property of the solutions, the variations have to be constrained accordingly. If these constraints are expressed by Lagrange multipliers, one obtains additional terms in the field equations which are of exactly the same kind as those dropped in the original variational principle. The Lagrange multipliers have to be chosen in such a way that the original variational principle is reestablished. The advantage of Lagrange multipliers consists in the fact that the variations can be taken for the reduced varia-

tional principle in the same way as for the original unconstrained problem. On the other hand, using the original action for nonorthonormal wave functions, the subsequent determination of Lagrange multipliers can be avoided. It is also noted that the role of Lagrange multipliers in the time-independent Hartree-Fock theory has been discussed in early work by Koopmans [7] and by Slater [8]. A detailed comparison of our time-dependent results with this work is made in Sec. III.

Our basic purpose in this work is a systematic discussion of the variational principle for the TDHF equations with orthonormality constraints. We restrict attention to systems that can be described by a single Slater determinant. After a brief statement of the variational principle in Sec. II A, a generalized set of TDHF equations is derived from the N-body action in Sec. II B and the conservation of the norm of the wave function in the TDHF approximation is demonstrated in this context. It is further shown that the solutions of these equations can be chosen orthonormal and a set of evolution equations for orthonormal functions is derived in Sec. II C. These equations contain time-dependent parameters that exactly correspond to the Lagrange multipliers of a variational principle with orthonormality constraints presented in Sec. II D. The physical significance of the Lagrange multipliers is discussed in Sec. III. It is demonstrated that the standard TDHF equations without Lagrange multipliers can be obtained by a unitary transformation of the function system. The major result of this analysis is a correction to the Slater determinant by a time-dependent phase factor that properly accounts for the mean interaction energy between the particles.

II. N-ELECTRON SYSTEMS

We consider an N-electron system, whose Hamiltonian takes the form

$$H(1,\ldots,N,t)=\sum_j H^{(1)}(j,t)+\sum_{j<k} H^{(2)}(j,k). \quad (2.1)$$

$H^{(1)}(j,t)$ represents a generally time-dependent single-particle Hamiltonian acting on the coordinates of particle j and $H^{(2)}(j,k)$ a pair-interaction Hamiltonian acting on the coordinates of two particles j and k. The sums are extended over all electrons and over all pairs of electrons, respectively. The coordinates of particle j include the spatial coordinates r_j and a spin-quantum number $m_{sj}=\pm\frac{1}{2}$. For simplicity of notation, we will use the abbreviations

$$j\equiv(r_j,m_{sj}), \quad \int dj\equiv\sum_{m_{sj}}\int d^3r_j. \quad (2.2)$$

In accordance with the general principles of quantum mechanics, the Hamiltonian is assumed to be Hermitian and symmetric with respect to an exchange of particles. More specific properties of the Hamiltonian are not required for the present purposes. It is mentioned, however, that we are mainly interested in the interaction of atoms with time-dependent laser fields [9], where the Hamiltonian assumes the explicit form

$$H^{(1)}(j,t)=-\frac{1}{2}\Delta_j+V(j,t), \quad (2.3a)$$

$$H^{(2)}(j,k)=H^{(2)}(k,j)=\frac{1}{|r_j-r_k|}. \quad (2.3b)$$

Here $V(j,t)=V_A(j)+r_j\cdot E(t)$ includes the atomic potential $V_A(j)$ and the time-dependent dipole interaction energy with an external electric field $E(t)$. The time evolution of the exact N-particle wave function is governed by the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(1,\ldots,N,t)=H(1,\ldots,N,t)\psi(1,\ldots,N,t). \quad (2.4)$$

A. Variational principle for the wave function

The time-dependent Schrödinger equation can be derived from a well-known variational principle,

$$\delta S[\psi,\psi^*]=0, \quad (2.5)$$

where the action S is defined as a functional of the function ψ and its complex conjugate ψ^* by

$$S[\psi,\psi^*]=(\psi,\mathcal{L}\psi) \quad \text{with} \quad \mathcal{L}=H-i\frac{\partial}{\partial t}. \quad (2.6)$$

Here and in the following we use the notation

$$(\phi,\psi)(s+1,\ldots,N,t)$$

$$\equiv\prod_{j=1}^{s}\int dj\,\phi^*(1,\ldots,N,t)\psi(1,\ldots,N,t),$$

$$(2.7a)$$

$$(\phi,\psi)(t)\equiv\prod_{j=1}^{N}\int dj\,\phi^*(1,\ldots,N,t)\psi(1,\ldots,N,t),$$

$$(2.7b)$$

$$(\phi,\psi)\equiv\int dt(\phi,\psi)(t). \quad (2.7c)$$

The product (2.7a) is defined by the integration of $\phi^*\psi$ over a subspace of s particles. The arguments of the brackets indicate the remaining variables after integration. For $s=N$ one obtains the usual scalar product (2.7b) in the N-particle Hilbert space, which still depends on time. A further time integration of this scalar product, as defined in Eq. (2.7c), is required to form the action (2.6) for the time-dependent Schrödinger equation. A corresponding notation will be used for functions, depending only on the coordinates of one or two particles,

$$(\phi,\psi)(t)=\int di\,\phi^*(i,t)\psi(i,t), \quad (2.8a)$$

$$(\phi,\psi)(i,t)=\int dj\,\phi^*(i,j,t)\psi(i,j,t). \quad (2.8b)$$

The variations of the fields ψ and ψ^* are assumed to vanish on the boundary of the $(3N+1)$-dimensional integration region to avoid boundary terms from partial integrations. Formal variation of the action (2.6) with respect to the functions ψ^* and ψ yields the Schrödinger equation and its adjoint,

$$\mathcal{L}\psi=0, \quad (\mathcal{L}^+\psi)^*=0, \qquad (2.9)$$

respectively. Since $\mathcal{L}$ is Hermitian with respect to the scalar product in the $(3N+1)$-dimensional space,

$$(\phi,\mathcal{L}^+\psi)=(\psi,\mathcal{L}\phi)^*=(\mathcal{L}\psi,\phi)^*=(\phi,\mathcal{L}\psi), \quad (2.10)$$

the adjoint equation can be dropped. The variational principle therefore determines the solutions of the time-dependent Schrödinger equation.

B. Variational principle for a single Slater determinant

The variational principle is advantageous for determining approximate solutions of the Schrödinger equation for a given set of trial functions. In the framework of the time-dependent Hartree-Fock theory, the N-particle wave function is approximated by a Slater determinant

$$\psi_s=\frac{1}{\sqrt{N!}}\sum_\pi \text{sgn}(\pi)\prod_{j=1}^N u_{\pi(j)}(j,t) \qquad (2.11)$$

of single-electron orbitals $u_k(j,t)$. Without explicit notation, the single-electron orbitals are understood as products of a spatial orbital and a spin wave function. The subscript k enumerates different functions and the argument j different particles. The sum is extended over all permutations π of the ordered set $1,\ldots,N$. The Slater determinant is completely antisymmetric with respect to an exchange of particles by requiring that $\text{sgn}(\pi)=+1$ for even and $\text{sgn}(\pi)=-1$ for odd permutations.

The summation over permutations can be performed in the left argument of Eq. (2.6) by noting that all $N!$ permutations give rise to the same contribution. Due to the symmetry $H(\pi(1),\ldots,\pi(N),t)=H(1,\ldots,N,t)$ of the Hamiltonian, one obtains

$$S[\psi_s,\psi_s^*]=\sqrt{N!}\left(\prod_{j=1}^N u_j(j,t),\mathcal{L}\psi_s\right). \qquad (2.12)$$

In common treatments of the time-dependent Hartree-Fock theory the N-particle functional S is further reduced to a sum of 1-particle and 2-particle functionals by assuming orthonormality of the functions $u_j(j,t)$. The constraint imposed on the variations by the orthonormality condition is neglected. Here we depart from this procedure, by first calculating the variation of the N-particle functional according to the exact variational principle and then applying the orthonormality condition. With the help of Eq. (2.10), variation with respect to $u_j(j,t)^*$ yields,

$$\delta S[\psi_s,\psi_s^*]=\sqrt{N!}\sum_{i=1}^N\left(\delta u_i(i,t)\prod_{j\neq i} u_j(j,t),\mathcal{L}\psi_s\right). \quad (2.13)$$

Considering arbitrary independent variations $\delta u_j(j,t)^*$, the variational principle implies,

$$\left(\prod_{j\neq i} u_j(j,t),\mathcal{L}\psi_s\right)(i,t)=0, \qquad (2.14)$$

where the integration is over the $3(N-1)$-dimensional subspace, excluding the time coordinate and the coordinates of electron i. In general, the Schrödinger equation will no longer be satisfied in the whole N-particle Hilbert space. Only the projections on single-particle subspaces, given by Eq. (2.14), can be made to vanish with trial functions of the form (2.11).

Using again Eq. (2.11) for the right argument in Eq. (2.14), one obtains the general form of the time-dependent Hartree-Fock equations,

$$\sum_\pi \text{sgn}(\pi)\left(\prod_{j\neq i} u_j(j,t),\mathcal{L}\prod_{j\neq i} u_{\pi(j)}(j,t)\right)(i,t)u_{\pi(i)}(i,t)=0. \qquad (2.15)$$

The set of equations for $i=1,\ldots,N$ determines the time evolution of the set of unknown functions $u_i(i,t)$.

For quantum mechanical systems, the norm of the wave function has to be conserved in time. It is therefore essential that the TDHF approximation fulfills a conservation law for the norm of the wave function. This property can be generally demonstrated by noting that

$$\left(\psi_s,i\frac{\partial\psi_s}{\partial t}\right)(t)=\sqrt{N!}\left(\prod_{j=1}^N u_j,i\frac{\partial\psi_s}{\partial t}\right)(t)$$

$$=\sqrt{N!}\left(\prod_{j=1}^N u_j,H\psi_s\right)(t)$$

$$=(\psi_s,H\psi_s)(t), \qquad (2.16)$$

where, in the second step, it has been assumed that ψ_s is a solution of the TDHF equations (2.14). Using this expression and its complex conjugate, it follows that the norm of the Slater determinant is conserved within the TDHF approximation for a Hermitian Hamiltonian H,

$$\frac{d}{dt}(\psi_s,\psi_s)(t)=i(H\psi_s,\psi_s)(t)-i(\psi_s,H\psi_s)(t)=0. \qquad (2.17)$$

C. Orthonormal functions

The TDHF equations can be further simplified by noting an ambiguity in the definition of the functions u_j. Under arbitrary linear, in general time, and space dependent transformations,

$$u_i'=\sum_k A_{ik}u_k \qquad (2.18)$$

with the property that

$$\det A=1, \qquad (2.19)$$

the Slater determinant,

$$\psi_s'=\det|u_i'(j)|=\det A\det|u_k(j)|=\det|u_k(j)|=\psi_s \qquad (2.20)$$

remains invariant. The transformed functions u_i' represent the same physical state as the original functions u_i. As a consequence, the basic TDHF equations (2.14) remain form-invariant under these transformations. Considering time-dependent transformations only, it is possible to choose a set of orthonormal functions U_i, satisfying

$$(U_i, U_j)(t) = \delta_{ij}. \qquad (2.21)$$

These are N^2 equations for $2[N(N-1)/2] + N = N^2$ real parameters of the Hermitian matrix (U_i, U_j). The complex matrix A_{ik} contains $2N^2$ real parameters, which are sufficient to satisfy N^2 orthonormalization conditions. The remaining N^2 parameters of A_{ik} correspond to arbitrary unitary transformations of the orthonormal system. If one of these parameters is fixed by the requirement (2.19), one can still perform arbitrary unitary transformations with determinant 1, which form the group SU(N) with $N^2 - 1$ real parameters.

This analysis shows that the present TDHF equations apply in the same form both to orthonormal and nonorthonormal function systems. To obtain orthonormal solutions U_i from the evolution equations (2.15) themselves, one therefore has to explicitly impose the orthonormality condition (2.21) at each instant of time. To ensure that the orthonormality condition remains valid in the course of time evolution, it is useful to demand

$$i\frac{d}{dt}(U_i, U_j)(t) = \left(U_i, i\frac{\partial U_j}{\partial t}\right)(t) - \left(i\frac{\partial U_i}{\partial t}, U_j\right)(t) = 0. \qquad (2.22)$$

For orthonormal functions, the sum over permutations in Eq. (2.15) can easily be evaluated by noting that most bracket terms vanish. Specifically, the following identities hold,

$$\left(\prod_{j\neq i} U_j(j), \prod_{j\neq i} U_{\pi(j)}(j)\right)(t) = \prod_{j\neq i} \delta_{\pi(j)j}, \qquad (2.23a)$$

$$\left(\prod_{j\neq i,k} U_j(j), \prod_{j\neq i,k} U_{\pi(j)}(j)\right)(t) = \prod_{j\neq i,k} \delta_{\pi(j)j}, \qquad (2.23b)$$

$$\left(\prod_{j\neq i,k,l} U_j(j), \prod_{j\neq i,k,l} U_{\pi(j)}(j)\right)(t) = \prod_{j\neq i,k,l} \delta_{\pi(j)j}. \qquad (2.23c)$$

In other words, the only nonvanishing permutations are those that permute only those particles excluded from the product states in Eq. (2.23). Applying this property of the brackets to the contributions from the Hamiltonian $H^{(1)}$, one finds,

$$\sum_{\pi} \text{sgn}(\pi)\left(\prod_{j\neq i} U_j(j,t), \sum_k H^{(1)}(k,t)\right.$$

$$\left.\times\prod_{j\neq i} U_{\pi(j)}(j,t)\right)(i,t)U_{\pi(i)}(i,t)$$

$$= H^{(1)}(i,t)U_i(i,t) + \sum_{k\neq i}\sum_{\pi'} \text{sgn}(\pi')(U_k, H^{(1)}$$

$$\times U_{\pi'(k)})(t)U_{\pi'(i)}(i,t), \qquad (2.24)$$

where π' refers to the two possible permutations of the set i, k. Corresponding contributions are obtained from the time derivative,

$$\sum_{\pi} \text{sgn}(\pi)\left(\prod_{j\neq i} U_j(j,t), \frac{\partial}{\partial t}\prod_{j\neq i} U_{\pi(j)}(j,t)\right)(i,t)U_{\pi(i)}(i,t)$$

$$= \frac{\partial}{\partial t}U_i(i,t) + \sum_{k\neq i}\sum_{\pi'} \text{sgn}(\pi')\left(U_k, \frac{\partial}{\partial t}\right.$$

$$\left.\times U_{\pi'(k)}\right)(t)U_{\pi'(i)}(i,t). \qquad (2.25)$$

According to the derivation of Eq. (2.15), the time derivative in the first line also acts on the function $U_{\pi(i)}(i,t)$ outside the bracket. In the following, however, this term has been separated and the remaining time derivatives are restricted to functions inside the brackets.

Finally, the contributions arising from $H^{(2)}$ can be divided into two parts by writing

$$\sum_{j<k} H^{(2)}(j,k) = \sum_{k\neq i} H^{(2)}(k,i) + \sum_{j<k, j\neq i, k\neq i} H^{(2)}(j,k). \qquad (2.26)$$

The first part can be treated in the same manner as $H^{(1)}$, depending only on the coordinates of one particle in the integration region. The second part yields

$$\sum_{j<k, j\neq i, k\neq i}\sum_{\pi''} \text{sgn}(\pi'')(U_j U_k, H^{(2)}$$

$$\times U_{\pi''(j)} U_{\pi''(k)})(t)U_{\pi''(i)}(i), \qquad (2.27)$$

where the summation over π'' denotes the six possible permutations of the set i,j,k.

To simplify notation, it is convenient to introduce the following definitions,

$$F(j,t) = H^{(1)}(j,t) - i\frac{\partial}{\partial t}, \qquad (2.28a)$$

$$G_{kl}(i,t) = (U_k(j,t), H^{(2)}(i,j)U_l(j,t))(i,t), \qquad (2.28b)$$

$$F_{kl}(t) = (U_k(j,t), F(j,t)U_l(j,t))(t), \qquad (2.28c)$$

$$M_{ij,kl}(t) = (U_i(i,t)U_j(j,t), H^{(2)}(i,j)U_k(i,t)U_l(j,t))(t). \qquad (2.28d)$$

$F(i,t)$ and $G_{kl}(i,t)$ are time-dependent Hermitian operators acting on the coordinates of particle i. The Hermiticity property of these operators is expressed by

$$F_{lk}(t) = F_{kl}^*(t), \qquad M_{kl,ij}(t) = M_{ij,kl}^*(t). \qquad (2.29)$$

It follows from the Hermiticity of $H^{(1)}$ and $H^{(2)}$ and from the orthonormalization condition (2.22). For later use we will also define an antisymmetrized matrix

$$M_{ij,\{kl\}} = M_{ij,kl} - M_{ij,lk} \qquad (2.30)$$

with the properties,

$$M_{kl,\{ij\}}=M^*_{ij,\{kl\}},\quad M_{ij,\{kl\}}=M_{ji,\{lk\}},$$

$$M_{ii,\{kl\}}=M_{ij,\{kk\}}=0. \tag{2.31}$$

The latter follow immediately from the Hermiticity and symmetry of H^2 and the antisymmetry of Eq. (2.30), respectively.

Using Eqs. (2.24), (2.25), (2.27), and (2.28) the time-dependent Hartree-Fock equations (2.15) can be rewritten in the form

$$F(i,t)U_i(i,t)+\sum_{j\neq i}\sum_{\pi'}\,\mathrm{sgn}(\pi')[F_{j\pi'(j)}(t)+G_{j\pi'(j)}(i,t)]$$

$$\times U_{\pi'(i)}(i,t)+\sum_{j<k,j\neq i,k\neq i}\sum_{\pi''}\,\mathrm{sgn}(\pi'')$$

$$\times M_{jk,\pi''(j)\pi''(k)}(t)U_{\pi''(i)}(i,t)=0. \tag{2.32}$$

The first term represents the one-electron Schrödinger equa-

tion for electron i. The second term contains the average interaction G_{jj} of electron i with electron j and a corresponding exchange contribution G_{ji}. These terms agree with the standard TDHF equations derived from the reduced two-body action. In addition, Eq. (2.32) includes time-dependent energy corrections for particle i due to changes in the single-electron energies $F_{jj}(t)$ and interaction energies $M_{jk,jk}(t)$ of the remaining particles. Note that the last term, containing the energies $M_{jk,jk}(t)$, is only present when the system consists of more than two particles.

As shown in the Appendix, the contributions from the various permutations in Eq. (2.32) can be rearranged in the form

$$FU_i+\sum_j\,G_{jj}U_i-G_{ji}U_j=\sum_j\,\mu_{ji}U_j \tag{2.33}$$

with the time-dependent coefficients

$$\mu_{ji}(t)=\begin{cases}-\sum_{j,j\neq i}F_{jj}-\sum_{j<k}M_{jk,\{jk\}}+\sum_{j,j\neq i}M_{ij,\{ij\}} & \text{for } i=j,\\[2mm] F_{ji}+\sum_k M_{jk,\{ik\}} & \text{for } i\neq j.\end{cases} \tag{2.34}$$

The standard TDHF equations correspond to the case where $\mu_{ij}=0$. In Sec. III, it will be shown that this form actually can be obtained by a unitary transformation of the spin orbitals with a time-dependent phase correction to the Slater determinant. In the next section an alternative derivation of Eq. (2.33) will be given, showing that the coefficients $\mu_{ij}(t)$ are the Lagrange multipliers of a variational principle with orthonormality constraints.

D. Variational principle with orthonormality constraints

Since the spin orbitals can always be chosen orthonormal, it is sufficient to perform variations within the subset of functions satisfying the orthonormality constraint (2.21). Using the method of Lagrange multipliers, this can be achieved by a variation of the modified action,

$$\tilde{S}=S-\int dt\sum_{i,j}\{(U_i,U_j)(t)-\delta_{ij}\}\mu_{ji}(t), \tag{2.35}$$

with

$$S=\int dt\sum_i F_{ii}+\sum_{i<j}M_{ij,\{ij\}}. \tag{2.36}$$

The reduced action (2.36) is obtained by using Eq. (2.21) in Eq. (2.12). Lagrange multipliers $\mu_{ij}(t)$ have been introduced for each constraint at each time t. Since $(U_i,U_j)(t)$ is Hermitian, the matrix of the Lagrange multipliers has the same property, $\mu_{ij}(t)=\mu^*_{ji}(t)$. From the variational principle $\delta\tilde{S}$

$=0$ with respect to variations of the functions U^*_i one immediately obtains the TDHF equations in the form

$$FU_i+\sum_j\,G_{jj}U_i-G_{ji}U_j=\sum_j\,\mu_{ji}U_j. \tag{2.37}$$

Taking now the projection on a function U_k, the Lagrange multipliers can be explicitly expressed as,

$$\mu_{ki}=F_{ki}+\sum_j M_{kj,\{ij\}}. \tag{2.38}$$

To eliminate the Lagrange multipliers, one has to impose conditions on these matrix elements from the complete variational principle. From the wave function ψ and the Schrödinger operator $\mathcal{L}$, one can only form a single scalar product that contains the matrix elements of Eq. (2.38),

$$(\psi,\mathcal{L}\psi)(t)=(\psi_s,\mathcal{L}\psi_s)(t)=\sum_i F_{ii}(t)+\sum_{i<j}M_{ij,\{ij\}}(t)=0. \tag{2.39}$$

This identity can be viewed as a condition on the time-dependent single-particle energies

$$E_i\equiv\left(U_i,i\frac{\partial}{\partial t}U_i\right)(t) \tag{2.40}$$

defined by the TDHF orbitals. Using Eq. (2.28a) in Eq. (2.39) it follows that the sum

$$\sum_i E_i = \sum_i (U_i, H^{(1)}U_i)(t) + \sum_{i<j} M_{jk,\{jk\}} = (\psi_s, H\psi_s)(t) \tag{2.41}$$

has to be equal to the expectation value of the energy in the quantum state ψ_s.

This relationship determines the trace of the matrix μ_{ij} as,

$$\mathrm{Tr}\{\mu\} = \sum_i F_{ii} + \sum_{ij} M_{ij,\{ij\}} = \sum_{j<k} M_{jk,\{jk\}}. \tag{2.42}$$

The remaining $N^2 - 1$ parameters from the Hermitian matrix μ_{ij} can be arbitrarily chosen. In particular, the full set of TDHF equations (2.33) imposes no conditions on the off-diagonal elements, as can be seen by comparing them with the identical expressions in Eq. (2.34).

III. DISCUSSION OF RESULTS

In the present work we have considered the variational principle for the TDHF equations for a Slater determinant. It has been shown that the variation of the complete N-body action leads to additional time-dependent parameters in the standard TDHF equations for orthonormal spin orbitals. These parameters agree with the Lagrange multipliers in a variational principle with orthonormality constraints on the spin orbitals. We now further discuss the significance of the Lagrange multipliers in the TDHF equations.

The Lagrange multipliers μ_{ij} form a Hermitian matrix with N^2 independent parameters. Since a unitary transformation has just the same number of parameters, all Lagrange multipliers can be removed at each time by a time-dependent unitary transformation, which will lead to the standard TDHF equations. We now demonstrate in detail the existence of such a unitary transformation and calculate its determinant, which is a complex number with unit magnitude. This determinant is required to obtain the corresponding transformation of the Slater determinant.

Consider a new set of spin-orbitals U'_m related to the old set U_i by a time-dependent unitary transformation T,

$$U'_m = \sum_i T_{im} U_i, \qquad U_i = \sum_m T^+_{mi} U'_m, \tag{3.1}$$

with

$$T_{im} = (U_i, U'_m)(t), \qquad T^+_{mi} = (U'_m, U_i)(t) = T^*_{im}.$$

The corresponding transformation of the Lagrange multipliers (2.38) is given by

$$\mu'_{nm} = \sum_{ij} T^+_{ni} \mu_{ij} T_{jm} - T^+_{ni} \delta_{ij} i \frac{\partial}{\partial t} T_{jm}. \tag{3.2}$$

If the transformation is time independent, the Lagrange multipliers transform as a tensor. However, for time-dependent transformations an additional term arises from the time-derivative in the operator $F = H^{(1)} - i(\partial/\partial t)$. Requiring that the transformed Lagrange multipliers μ'_{nm} vanish, $T_{jm}(t)$ has to satisfy the evolution equation,

$$i\frac{\partial}{\partial t} T_{im}(t) = \sum_j \mu_{ij}(t) T_{jm}(t). \tag{3.3}$$

Suppose that the Lagrange multipliers have already been removed at time t_n. In a subsequent infinitesimal time interval Δt the solution of Eq. (3.3) is given by the unitary operator

$$T(\Delta t) = e^{-i\mu(t_n)\Delta t}. \tag{3.4}$$

By repeated application of this procedure at subsequent times $t_n = n\Delta t$, $n = 1,2,3,\ldots$, one can obtain the unitary transformation for a finite time interval in the form,

$$T(t) = \prod_n e^{-i\mu(t_n)\Delta t}. \tag{3.5}$$

The determinant of this transformation can be obtained by noting that

$$\det B = e^{-i\,\mathrm{Tr}\{A\}} \tag{3.6}$$

for any unitary operator $B = e^{-iA}$ [10]. This relationship holds in the basis of eigenstates of the Hermitian operator A and it follows generally from the invariance of the trace and the determinant with respect to unitary transformations. Using Eq. (3.6) yields

$$\det T(t) = \prod_n \exp[-i\,\mathrm{Tr}\{\mu(t_n)\}\Delta t_n]$$

$$= \exp\left[-i\int dt\,\mathrm{Tr}\{\mu(t)\}\right]$$

$$= \exp\left[-i\int dt \sum_{j<k} M_{jk,\{jk\}}\right]. \tag{3.7}$$

In the last step, the trace of the matrix $\mu_{ij}(t)$ has been expressed by the average interaction energy between all pairs of particles according to Eq. (2.42). Eliminating the Lagrange multipliers by this set of basis functions, the TDHF equations assume their standard form

$$i\frac{\partial}{\partial t} U'_i = H^{(1)} U'_i + \sum_j G'_{jj} U'_i - G'_{ji} U'_j. \tag{3.8}$$

The matrix elements G'_{ij} are defined by Eq. (2.28b) in terms of the functions U'_i. The Slater determinant ψ_s for the physical wave function can be obtained from the Slater determinant ψ'_s of the solution U'_i by the unitary transformation

$$\psi_s = \frac{1}{\det T}\psi'_s = \exp\left[i\int dt\sum_{j<k} M_{jk,\{jk\}}\right]\psi'_s. \tag{3.9}$$

This phase factor has to be included in the time-dependent solution of the wave function after the standard TDHF equations have been solved.

The appearance of an additional phase can be simply understood by noting that the phase shift (3.9) corresponds to an energy difference

$$E' - E = \left(\psi_s', i\frac{\partial}{\partial t}\psi_s' \right)(t) - \left(\psi_s, i\frac{\partial}{\partial t}\psi_s \right)(t) = \sum_{j<k} M_{jk,\{jk\}}$$
$$(3.10)$$

between the energies E' and E calculated with ψ_s' and ψ_s, respectively. The physical energy of the system is defined by the expectation value of the Hamiltonian with the wave function ψ_s, yielding

$$E = \left(\psi_s, i\frac{\partial}{\partial t}\psi_s \right)(t) = (\psi_s, H\psi_s)(t)$$

$$= \sum_i (U_i, H^{(1)}U_i)(t) + \sum_{i<j} M_{ij,\{ij\}}. \qquad (3.11)$$

On the other hand, the energy E' can be calculated as a sum of single-electron energies,

$$E' = \left(\psi_s', i\frac{\partial}{\partial t}\psi_s' \right)(t) = \sum_i \left(U_i', i\frac{\partial}{\partial t}U_i' \right)(t), \quad (3.12)$$

which are given by the solution of the TDHF equations (3.8) as,

$$E_i' \equiv \left(U_i', i\frac{\partial}{\partial t}U_i' \right)(t) = (U_i', H^{(1)}U_i')(t) + \sum_j M_{ij,\{ij\}}. \qquad (3.13)$$

Inserting Eq. (3.13) into Eq. (3.12), it follows that the interaction energy is counted twice in E'. The double counting of the interaction energy in the standard TDHF model is corrected by the phase factor to the wave function in Eq. (3.9).

It may also be of interest to compare the present results with those of the time-independent Hartree-Fock theory for a single Slater determinant. In the time-independent framework, the role of Lagrange multipliers has been discussed by Koopmans [7] and an extended discussion of the time-independent theory can be found in the book of Slater [8]. The time-independent HF equations can be obtained from the present TDHF equations by considering a time-independent Hamiltonian and assuming stationary states with the time dependence

$$i\frac{\partial}{\partial t}U_i = E_i U_i. \qquad (3.14)$$

With this substitution, one obtains from Eq. (2.37) the HF equations

$$H^{(1)}U_i + \sum_j G_{jj}U_i - G_{ji}U_j = i\frac{\partial}{\partial t}U_i + \sum_j \mu_{ji}U_j$$

$$= \sum_j \lambda_{ji}U_j, \qquad (3.15)$$

where

$$\lambda_{ij} = (U_i, H^{(1)}U_j) + \sum_k M_{ik,\{jk\}}. \qquad (3.16)$$

The matrix λ_{ij} represents the matrix of Lagrange multipliers in the time-independent theory introduced by Koopmans [7]. In the work of Slater, these parameters have been defined with the opposite sign [8].

In the time-independent theory it is always possible to choose a set of functions that diagonalize λ_{ij},

$$\sum_j \lambda_{ji}U_j' = E_i'U_i'. \qquad (3.17)$$

The specific set of functions U_i' that diagonalizes λ_{ij} has been called a characteristic system [7]. The unitary transformation introduced above in the time-dependent framework is a generalization of this diagonalization procedure. In the time-independent case, the condition for setting $\mu_{ij}' = \lambda_{ij}' - E_i'\delta_{ij} = 0$ agrees with Eq. (3.17).

The condition (2.42) on the trace of the Lagrange multipliers assumes the time-independent form

$$\text{Tr}\{\mu\} = \text{Tr}\{\lambda\} - \sum_i E_i = \sum_i E_i' - E_i = E' - E = \sum_{i<j} M_{ij,\{ij\}},$$
$$(3.18)$$

where the trace of λ has been evaluated without restriction by the set of functions U_i'. The discrepancy between the energies E' and E is well known in the time-independent theory. In the present work we draw attention to the fact that one has to take into account a corresponding phase change of the wave function, which is particularly relevant in the time-dependent context.

It is finally noted that the energies E_i' in the standard form of the HF equations have a physical meaning that is given by Koopmans' theorem [7]. It states that the energy required to remove the electron i from the system without changing the remaining orbitals is equal to $-E_i'$. The energies of the N-electron system and the $(N-1)$-electron system are physically well defined. It can easily be shown that their difference is given by expression (3.13), which represents the single-electron energy of electron i and the interaction energy of electron i with all the other particles. Koopmans' theorem remains valid in the time-dependent case, if the energies $E_i'(t)$ are defined by Eq. (3.13).

IV. CONCLUSION

The TDHF theory for a Slater determinant of an N-electron Coulomb system has been reviewed in the context of a variational principle for the N-body action. It is found that the Slater determinant calculated by standard TDHF equations has to be corrected by a time-dependent phase factor. This factor properly accounts for the mean interaction energy of the system, which otherwise would be calculated twice by summing over single-particle energies. In principle, the phase correction to the wave function may be observable, e.g., by measurements of the polarizability of an atom in a superposition of quantum states.

APPENDIX: COUPLING COEFFICIENTS

The coupling coefficients $\mu_{ij}(t)$ in Eq. (2.33) can be obtained in the following way. Using the definition (2.30), the sum over the permutations π'' in Eq. (2.32) can be written as,

$$\sum_{\pi''} \text{sgn}(\pi'') M_{jk,\pi''(j)\pi''(k)} U_{\pi''(i)}(i)$$
$$= M_{jk,\{jk\}} U_i + M_{jk,\{ki\}} U_j + M_{jk,\{ij\}} U_k. \quad \text{(A1)}$$

Noting the properties (2.31), the restricted sum of the first term over j and k can be evaluated as,

$$\sum_{j<k,j\neq i,k\neq i} M_{jk,\{jk\}}$$
$$= \sum_{j<k} M_{jk,\{jk\}}(1-\delta_{ij})(1-\delta_{ik})$$
$$= \sum_{j<k} M_{jk,\{jk\}} - \sum_{k,i<k} M_{ik,\{ik\}} - \sum_{j,j<i} M_{ji,\{ji\}}$$
$$= \sum_{j<k} M_{jk,\{jk\}} - \sum_{j,j\neq i} M_{ij,\{ij\}}. \quad \text{(A2)}$$

Together with the contributions from the identical permutation in the sum over π', there follow the diagonal elements $\mu_{ii}(t)$ as given by Eq. (2.33). The sum over the remaining two terms in Eq. (A1) can be written as,

$$\sum_{j<k,j\neq i,k\neq i} M_{jk,\{ki\}} U_j + M_{jk,\{ij\}} U_k$$
$$= \sum_{j<k,j\neq i,k\neq i} M_{jk,\{ki\}} U_j + \sum_{k<j,j\neq i,k\neq i} M_{kj,\{ik\}} U_j$$
$$= \sum_{j,k,j\neq i} M_{jk,\{ki\}} U_j = -\sum_{j,k} M_{jk,\{ik\}} U_j. \quad \text{(A3)}$$

Together with the exchange contributions from the sum over π', one obtains the off-diagonal elements $\mu_{ji}(t)$, $i\neq j$ of Eq. (2.33).

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