# Three-dimensional statistical reduction of the *N*-body Schrödinger equation for electrons with pairwise Coulomb interactions

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Based on a second-quantized representation of the nonrelativistic Hamiltonian of a system of $N$ electrons with pairwise Coulomb interactions, we demonstrate the exact statistical reduction of the $N$-body problem to a three-dimensional Schrödinger equation for the motion of a single active electron with all other $N-1$ electrons acting as spectators. As a by-product, three-dimensional Schrödinger equations for the ground and excited states of two-electron atoms and ions are derived and the dynamical role of Pauli's exclusion principle is established. The classical limit $\hbar \to 0$ of the quantal all-electron equations is examined, and the Thomas-Fermi equation including the Amaldi correction is obtained.

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## I. INTRODUCTION

The $N$-body problem is a central problem in the determination of the properties of atoms, molecules, nuclei, etc. [1,2]. The traditional approaches to the $N$-body problem are based on self-consistent Thomas-Fermi, Hartree, and Hartree-Fock methods, and more recently an alternative approach based on adiabatic hyper-spherical representation [3] has proven to provide good agreement with experimental observations [4]. In this work we demonstrate the exact statistical reduction of the $N$-electron problem with pairwise Coulomb interactions to a three-dimensional linear Schrödinger equation for the motion of a single active electron with the remaining $N-1$ electrons acting as spectators of its motion. We establish the covariance of this equation with respect to the Pauli's exclusion principle, which determines the motion of the spectator electrons. We consider in sufficient detail these equations for the case of two-electron atoms, where we express the Pauli's exclusion principle by a three-dimensional differential equation for the motion of a single active electron that acts on the state of its motion by inducing quantum transitions between the states of its partner.

The paper is organized as follows: Section II presents the derivation of three-dimensional nonrelativistic equations of motion for $N$ electrons, Sec. III applies these equations to the case of one and two-electron atoms, Sec. IV examines the classical limit ($\hbar \to 0$) of the these equations, in particular the Thomas-Fermi-Amaldi equation is derived, and Sec. V contains our main conclusions. Unless stated otherwise, we use atomic units ($e=\hbar=m_e=1$).

## II. DERIVATION OF EQUATIONS OF MOTION

The nonrelativistic Hamiltonian $H=T+U+V$ for a system of $N$ electrons with Coulomb interactions [5] is a sum of a kinetic energy,

$$T=\sum_{\sigma}\int d^3\mathbf{r}\,\psi_{\sigma}^{\dagger}(\mathbf{r})\left(-\frac{1}{2}\nabla^2\psi_{\sigma}(\mathbf{r})\right), \tag{1}$$

potential energy of the electrons in a given external one-body potential $v(\mathbf{r})$,

$$U=\sum_{\sigma}\int d^3\mathbf{r}\,v(\mathbf{r})\psi_{\sigma}^{\dagger}(\mathbf{r})\psi_{\sigma}(\mathbf{r}), \tag{2}$$

and the total two-electron Coulomb interaction energy

$$V=\frac{1}{2}\sum_{\sigma,\sigma'}\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{\sigma}^{\dagger}(\mathbf{r})\psi_{\sigma'}^{\dagger}(\mathbf{r}')\psi_{\sigma'}(\mathbf{r}')\psi_{\sigma}(\mathbf{r}), \tag{3}$$

where $\psi_{\sigma}(\mathbf{r})$ are the local Fermi-field operators that satisfy the Fermi-Dirac anticommutation relations

$$\{\psi_{\sigma}(\mathbf{r}),\psi_{\sigma'}^{\dagger}(\mathbf{r}')\}=\delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,\sigma'},\quad \{\psi_{\sigma}(\mathbf{r}),\psi_{\sigma'}(\mathbf{r}')\}=0, \tag{4}$$

and $\sigma$ denotes the projection of the electron spin on an arbitrary, but fixed spatial $z$ axis.

Let $|0\rangle$ be the ground the state of the interacting $N$-electron system in the Schrödinger picture. We write the necessary expressions for the three different contributions to the total ground-state energy, $E_0=\langle 0|T+U+V|0\rangle$. The expectation value of the kinetic energy is most easily expressed in momentum representation

$$T_e=\langle 0|T|0\rangle=\sum_{\mathbf{p},\sigma}\frac{\mathbf{p}^2}{2}\langle 0|c_{\mathbf{p},\sigma}^{\dagger}c_{\mathbf{p},\sigma}|0\rangle, \tag{5}$$

where $c_{\mathbf{p},\sigma}$ are the annihilation operators of electronic states with momentum $\mathbf{p}$ and spin component $\sigma$. We further introduce a complete set of known intermediate many-body states $|n\rangle$,

$$\sum_{n}|n\rangle\langle n|=\mathbf{1}, \tag{6}$$

which will be exactly specified later, and $\mathbf{1}$ is the unit operator in the Fock space for the fermions. By substituting Eq. (6) into Eq. (5) we express the expectation value of the kinetic energy,

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$$T_e = \sum_{n,\mathbf{p}\sigma} \frac{\mathbf{p}^2}{2} \psi_{n;\mathbf{p}\sigma} \psi^*_{n;\mathbf{p}\sigma}, \tag{7}$$

by means of yet unknown $N$-body amplitudes $\psi_{n;\mathbf{p}\sigma} = \langle n | c_{\mathbf{p},\sigma} | 0 \rangle$. Quite similarly, the potential energy of the electrons in the external field $v(\mathbf{r})$ is

$$U_e = \langle 0|U|0\rangle = \sum_{n,\mathbf{p}\sigma} \sum_{\mathbf{p}'} U(\mathbf{p}-\mathbf{p}') \psi_{n;\mathbf{p}\sigma} \psi^*_{n;\mathbf{p}'\sigma}. \tag{8}$$

By using the anticommutation relations between the Fermi operators, we obtain for the total ground-state Coulomb interaction energy $V_{ee} = \langle 0|V|0\rangle$

$$\frac{1}{2} \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \langle 0 | \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) \psi^\dagger_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') | 0 \rangle - \frac{1}{2} \left( \lim_{\mathbf{r}\to\mathbf{r}'} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right) N, \tag{9}$$

where the second term in Eq. (9) is divergent due to the singularity of the Coulomb potential at small distances; nevertheless, the divergent term is constant due to conservation of the number of electrons in the ground state, $N = \Sigma_\sigma \int d^3\mathbf{r} \langle 0 | \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) | 0 \rangle$. We will demonstrate later that this divergence is not physically relevant and continue with the calculation of the nondivergent part of the Coulombic energy as given by the first term in Eq. (9). By Fourier expanding the Coulomb potential and substituting the representation of the unit operator, Eq. (6), into Eq. (9), we obtain

$$V_{ee} = \frac{1}{2} \sum_{n,\mathbf{k}\sigma,\sigma'} \frac{4\pi}{\mathbf{k}^2} \int d^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \langle 0 | \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) | n \rangle \times \int d^3\mathbf{r}'\, e^{-i\mathbf{k}\cdot\mathbf{r}'} \langle n | \psi^\dagger_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') | 0 \rangle. \tag{10}$$

Equation (10) for $V_{ee}$ represents the Coulomb interactions of the quantum-mechanical fluctuations of the electron density in the ground state,

$$V_{ee} = \frac{1}{2} \sum_{n,\mathbf{k}\sigma,\sigma'} \rho_{0n}(-\mathbf{k},\sigma) \frac{4\pi}{\mathbf{k}^2} \rho_{n0}(\mathbf{k},\sigma'), \tag{11}$$

where the matrix representation of the density fluctuation operator at wave vector $\mathbf{k}$ is

$$\rho_{n0}(\mathbf{k},\sigma) = \sum_{\mathbf{q}} \langle n | c^\dagger_{\mathbf{q},\sigma} c_{\mathbf{q}+\mathbf{k},\sigma} | 0 \rangle = \sum_m \sum_{\mathbf{q}} \langle n | c^\dagger_{\mathbf{q},\sigma} | m \rangle \langle m | c_{\mathbf{q}+\mathbf{k},\sigma} | 0 \rangle.$$

It is important to observe that the representation of Eq. (12) for the density fluctuations involves a statistical Fermi-Dirac matrix $\alpha^*_{mn}(\mathbf{q},\sigma) = \langle m | c^\dagger_{\mathbf{q},\sigma} | n \rangle$ that does not depend on the nature of the Coulomb interactions and can be evaluated just once if the known intermediate many-body states $|n\rangle$ are specified. Therefore the fluctuations of the density are entirely representable by the unknown amplitudes $\psi_{n,\mathbf{p}\sigma}$:

$$\rho_{n0}(\mathbf{k},\sigma) = \sum_{m,\mathbf{q}} \alpha^*_{nm}(\mathbf{q},\sigma) \psi_{m,\mathbf{q}+\mathbf{k}\sigma}. \tag{12}$$

The Coulomb interaction energy as expressed in terms of the amplitudes $\psi_n$ is given by

$$V_{ee} = \frac{1}{2} \sum_{\mathbf{k}} \frac{4\pi}{\mathbf{k}^2} \sum_{n,m,m'} \sum_{\mathbf{q}\sigma,\mathbf{q}'\sigma'} \alpha_{m'n}(\mathbf{q}',\sigma') \alpha^*_{nm}(\mathbf{q},\sigma) \times \psi_{m,\mathbf{q}+\mathbf{k}\sigma} \psi^*_{m',\mathbf{q}'+\mathbf{k}\sigma'}. \tag{13}$$

The comparison of Eqs. (5), (8), and (13) demonstrates the fact that the total ground-state energy is entirely representable by the unknown amplitudes $\psi_{n,\mathbf{p}\sigma}$. We further invoke the Rayleigh-Ritz variational method and regard these unknown amplitudes as variational parameters that deliver the minimum of the total energy under the constraint of conservation of total number $N$ of particles in the ground state; i.e., we write the variational equation

$$\frac{\delta}{\delta \psi^*_{n,\mathbf{p}\sigma}} (T_e + U_e + V_{ee}) - \lambda \psi_{n,\mathbf{p}\sigma} = 0, \tag{14}$$

where $\lambda$ is unknown Lagrangian multiplier. When written explicitly, Eq. (14) reduces to a linear three-dimensional Schrödinger equation for a single active electron:

$$\frac{\mathbf{p}^2}{2} \psi_{n,\mathbf{p}\sigma} + \sum_{\mathbf{q}} U(\mathbf{q}-\mathbf{p}) \psi_{n,\mathbf{q}\sigma} - \lambda \psi_{n,\mathbf{p}\sigma} + \sum_{\mathbf{k},\mathbf{q}\lambda,m} V_{nm}(\mathbf{p}-\mathbf{k}\sigma;\mathbf{q}\lambda) \psi_{m,\mathbf{q}+\mathbf{k}\lambda} = 0, \tag{15}$$

where $U(\mathbf{k})$ is the Fourier component of the external one-body potential and the matrix elements $V_{nm}$ given by

$$V_{nm}(\mathbf{p}-\mathbf{k}\sigma;\mathbf{q}\lambda) = \frac{4\pi}{\mathbf{k}^2} [\langle n | c_{\mathbf{p}-\mathbf{k}\sigma} c^\dagger_{\mathbf{q}\lambda} | m \rangle - \langle n | m \rangle \delta(\mathbf{p}-\mathbf{k}-\mathbf{q}) \delta_{\sigma\lambda}]$$

represent the Coulomb potential felt by the active electron, but altered statistically by the presence of spectator electrons in intermediate quantum states $|n\rangle$. The last term in Eq. (16) subtracts the contributions from the disconnected terms that lead to divergent electron self-energy contributions of the form $\Sigma_{\mathbf{k}} 4\pi/\mathbf{k}^2$ in the total energy. These disconnected terms cancel out the divergences in Eq. (9).

We now specify the intermediate states $\{|n\rangle\}$ to be noninteracting many-body states that are the normalized eigenstates of the kinetic energy operator with fixed number $N$ of occupied one-electron states—i.e.,

$$|n\rangle = \prod_{i=1}^{N} c^\dagger_{\mathbf{p}_i,\sigma_i} |\mathrm{vac}\rangle, \tag{16}$$

where $|\mathrm{vac}\rangle$ is the noninteracting $N$-electron vacuum state. More precisely, the noninteracting representation is specified by the equations

$$|\mathrm{vac}\rangle = |0,0,\ldots\rangle, \quad c_{\mathbf{p}\sigma} |\mathrm{vac}\rangle = 0,$$

$$c_{\mathbf{p}\sigma} | \cdots n_{\mathbf{p}\sigma} \cdots \rangle = n^{1/2}_{\mathbf{p}\sigma} | \cdots 1 - n_{\mathbf{p}\sigma} \cdots \rangle$$

$$c^\dagger_{\mathbf{p}\sigma} | \cdots n_{\mathbf{p}\sigma} \cdots \rangle = (1 + n_{\mathbf{p}\sigma})^{1/2} | \cdots 1 + n_{\mathbf{p}\sigma} \cdots \rangle, \tag{17}$$

where $n_{\mathbf{p}\sigma} = \{0,1\}$ are the occupation numbers of plane-wave states with momentum $\mathbf{p}$ and projection $\sigma$ of the spin $s$

$=1/2$ on an arbitrary but fixed spatial $z$ axis. In this representation the $N$-body wave function $\psi_{n,\mathbf{p}\sigma}$ of the ground state of the interacting electrons is given by

$$\psi_{\{\mathbf{p}_i,\sigma_i\},\mathbf{p}\sigma} = \left(\prod_{i=1}^{N-1} c^{\dagger}_{\mathbf{p}_i,\sigma_i}|\mathrm{vac}\rangle\right)^{\dagger} c_{\mathbf{p}\sigma}|0\rangle, \tag{18}$$

in which only one electron with quantum numbers $(\mathbf{p},\sigma)$ is active, with the remaining electrons in the intermediate $(N-1)$-particle state act as spectators.

The generalization of the above scheme for excited many-body electronic states can be obtained in the same manner, since of the statistical factorization of the Coulomb Hamiltonian. The unknown excited-state amplitudes can be obtained rather as follows. Suppose we want to evaluate the first excited $N$-body energy level $E_1=\langle 1;N|H|1;N\rangle$ corresponding to the state $|1;N\rangle$. The representation of the excited-state amplitude is given by

$$\psi^{(1)}_{n,\mathbf{p}\sigma} = \left(\prod_{i=1}^{N-1} c^{\dagger}_{\mathbf{p}_i,\sigma_i}|\mathrm{vac}\rangle\right)^{\dagger} c_{\mathbf{p}\sigma}|1;N\rangle \tag{19}$$

and can be evaluated from the three-dimensional Schrödinger equation (15) under the constraints of orthogonality—i.e., $\langle 0;N|1;N\rangle=0$. These constraints can be imposed by taking trial wave function that is orthogonal to the ground-state wave function and next solve the three-dimensional Schrödinger equation for the active electron in the excited many-body state. For instance, the orthogonality constraints are imposed automatically if the wave functions of electronic states are chosen to be eigenfunctions of the total angular momentum $L$, its projection $M$ on a fixed spatial $z$ axis, and the total spatial parity $\lambda=\pm 1$.

## III. APPLICATION TO ONE- AND TWO-ELECTRON ATOMS

We apply the above formalism for one- and two-electron atoms and ions $N=1,2$. The momentum representation of the external potential of a point nucleus is given by $v(q)=-4\pi Z/q^2$ and $Z\geqslant 1$. For $N=1$, the wave function in Eq. (18) is the wave function of the active electron $\psi_{\mathbf{p}\sigma}=\langle \mathrm{vac}|c_{\mathbf{p},\sigma}|0;N=1\rangle$. The intermediate state is the noninteracting vacuum state $|n\rangle=|\mathrm{vac}\rangle$. The Fock matrix $V_{nm}$ of the effective one-electron potential vanishes. Therefore, the Schrödinger equation for the ground-state wave function reduces to

$$\frac{\mathbf{p}^2}{2}\psi_{\mathbf{p}\sigma} - \sum_{\mathbf{p}'}\frac{4\pi Z}{|\mathbf{p}-\mathbf{p}'|^2}\psi_{\mathbf{p}'\sigma} = \lambda\psi_{\mathbf{p}\sigma}. \tag{20}$$

The wave function $\psi_{\mathbf{p}\sigma}=\psi(\mathbf{p})\chi_\sigma$ is a product of orbital function $\psi_{\mathbf{p}}$ and normalized two-component spinor $\chi_\sigma$ as a consequence of the nonrelativistic approximation. Equation (20) exhibits the well-known solution for the ground-state wave function, $\psi=(Z^3/\pi)^{1/2}\exp(-Zr)$, with energy level $E_0=\lambda=-Z^2/2$.

The first nontrivial case is $N=2$, which corresponds to negative hydrogen anion $H^-$, helium atom He, and He-like ions. The intermediate state $|n\rangle=c^{\dagger}_{\mathbf{q}\lambda}|\mathrm{vac}\rangle$ is a plane-wave one-electron state. The matrix representation of the one-body Fermi-Dirac-Fock potential $V_{nm}$ felt by the active electron is

$$V_{\mathbf{p}'\sigma';\mathbf{q}'\lambda'}(\mathbf{p}-\mathbf{k}\sigma;\mathbf{q}\lambda) = -\frac{4\pi}{k^2}\delta(\mathbf{p}+\mathbf{k}-\mathbf{q}')\delta(\mathbf{p}'-\mathbf{q})\times\delta_{\lambda'\sigma}\delta_{\lambda\sigma'}; \tag{21}$$

therefore, the Schrödinger equation for the active electron becomes

$$\frac{\mathbf{p}^2}{2}\psi_{\mathbf{p}'\sigma',\mathbf{p}\sigma} - \sum_{\mathbf{q}}\frac{4\pi Z}{|\mathbf{p}-\mathbf{q}|^2}\psi_{\mathbf{p}'\sigma',\mathbf{q}\sigma} - \lambda\psi_{\mathbf{p}'\sigma',\mathbf{p}\sigma} + \sum_{\mathbf{k}}\frac{4\pi}{\mathbf{k}^2}\psi_{\mathbf{p}'-\mathbf{k}\sigma',\mathbf{p}+\mathbf{k}\sigma} = 0. \tag{22}$$

Equation (22) describes the motion of a single active electron altered both by the Coulomb potential of the fixed nucleus with charge $Z$ and by the spectator electron. The spectator radiates at wave vector $\mathbf{k}$ with recoil by changing its momentum to $\mathbf{q}-\mathbf{k}$; as a response, the active electron changes its momentum to $\mathbf{p}+\mathbf{k}$. The wave function is antisymmetric, $\psi_{\mathbf{p}'\sigma';\mathbf{p}\sigma}=-\psi_{\mathbf{p}\sigma;\mathbf{p}'\sigma'}$, in compliance with Pauli's exclusion principle, and the Schrödinger's equation is explicitly covariant with respect to exchange of the quantum numbers $(\mathbf{p},\sigma)\leftrightarrow(\mathbf{p}',\sigma')$ between the spectator and active electrons.

It is further instructive to write the equations of motion in coordinate representation, where we obtain

$$\left(-\frac{1}{2}\nabla^2-\frac{Z}{r}\right)\psi_{\mathbf{p}'\sigma'}(\mathbf{r},\sigma) - \lambda\psi_{\mathbf{p}'\sigma'}(\mathbf{r}\sigma) + \int d^3\mathbf{k}\frac{4\pi}{k^2}e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-\mathbf{k}\cdot\nabla_{\mathbf{p}'}}\psi_{\mathbf{p}'\sigma'}(\mathbf{r},\sigma) = 0. \tag{23}$$

The operator $\exp(-\mathbf{k}\cdot\nabla_{\mathbf{p}'})$ acts on the variables of the spectator by generating boost on a wave vector $-\mathbf{k}$, and $i\nabla_{\mathbf{p}'}=\mathbf{r}'$ is just the momentum representation of the displacement operator. The eigenvalues and eigenfunctions of the translation operator are given by the equation $e^{-\mathbf{k}\nabla_{\mathbf{p}'}}e^{-i\mathbf{p}'\cdot\mathbf{r}'}=e^{i\mathbf{k}\cdot\mathbf{r}'}e^{-i\mathbf{p}'\cdot\mathbf{r}'}$. Therefore by expanding the two-electron wave-function $\psi_{\mathbf{p}'}(\mathbf{r})$ over a complete set of plane-wave eigenstates of the translation operator—i.e., $\psi_{\mathbf{p}'}(\mathbf{r})=\int d^3\mathbf{r}'\,e^{-i\mathbf{p}'\cdot\mathbf{r}'}\psi_{\mathbf{r}'}(\mathbf{r})$—we obtain these equations in coordinate representation:

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}}-\frac{Z}{r}+\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)\psi_{\mathbf{r}'}(\mathbf{r}) = \lambda\psi_{\mathbf{r}'}(\mathbf{r}), \tag{24}$$

where we have dropped spinor indices by assuming the pair of electrons to be in a spin-singlet state. It is worth demonstrating how the Hartree-Fock equations follow from Eq. (24). By assuming that the two-electron wave function is representable by $\psi(\mathbf{r},\mathbf{r}')=\phi(\mathbf{r})\phi(\mathbf{r}')$, substituting this representation into Eq. (24), multiplying on the left by the conjugate wave function $\phi^*(\mathbf{r}')$, and integrating over the variables of the spectator, we obtain the equation

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{Z}{r}+\int d^3\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right)\phi(\mathbf{r})=\lambda\phi(\mathbf{r}), \quad (25)$$

where $n(\mathbf{r})=|\phi(\mathbf{r})|^2$ is the one-electron density. Therefore Eq. (24) reduces to the Hartree equation for the motion of one electron in a screened Coulomb potential and the Lagrangian multiplier has a meaning of one-electron binding energy.

The exact six-dimensional two-electron wave function of Eq. (24) is further expanded over

$$\psi_{\mathbf{r}'}(\mathbf{r})=\sum_n u_n(\mathbf{r}')\Phi_n(\mathbf{r};\mathbf{r}'), \quad (26)$$

one-electron eigenfunctions $\Phi_n$ of the two-center Coulomb Hamiltonian,

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{Z}{r}+\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)\Phi_n(\mathbf{r};\mathbf{r}')=\varepsilon_n(\mathbf{r}')\Phi_n(\mathbf{r};\mathbf{r}'), \quad (27)$$

where the displacement of the spectator electron $\mathbf{r}'$ is arbitrary but fixed. After solving the two-center problem for the functions $\Phi_n$, the unknown amplitudes $u_n$ can be obtained by exploiting the covariance of the Schrödinger's equation with respect to the Pauli's exclusion principle—i.e., by exchanging the places of the active and the spectator electrons:

$$\psi_{\mathbf{r}'}(\mathbf{r})=\psi_{\mathbf{r}}(\mathbf{r}')=\sum_n u_n(\mathbf{r})\Phi_n(\mathbf{r}';\mathbf{r}), \quad (28)$$

and substituting Eq. (28) into Eq. (24), we obtain a system of coupled equations of motion for the "new" active electron

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{Z}{r}-\lambda\right)u_n(\mathbf{r})+\sum_m W_{mn}(\mathbf{r})u_m(\mathbf{r})=0. \quad (29)$$

The nonadiabatic couplings $W_{mn}(\mathbf{r})=K_{mn}(\mathbf{r})+V_{mn}(\mathbf{r})$ describe effects of (i) the recoil of the "current" active electron that induces transitions in the two-center quantum states $|n\rangle$ of the "previous" active electron (which is now a spectator),

$$K_{mn}(\mathbf{r})=-\left[\langle m|\nabla_{\mathbf{r}}|n\rangle\cdot\nabla_{\mathbf{r}}+\frac{1}{2}\langle m|\nabla_{\mathbf{r}}^2|n\rangle\right], \quad (30)$$

and (ii) quantum transitions between the states of the spectator expressed by screened electron-electron Coulomb matrix elements $V_{mn}$ given by

$$V_{mn}(\mathbf{r})=\int d^3\mathbf{r}'\ \Phi_m^*(\mathbf{r}';\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\Phi_n^*(\mathbf{r}';\mathbf{r}). \quad (31)$$

Therefore as consequence of the Pauli's exclusion principle, the active electron determines the state of its motion by causing quantum transitions between the states of its partner.

## IV. THOMAS-FERMI APPROXIMATION

In this section, we consider the more general case of $N\geqslant 2$ electrons; in particular, we consider the classical limit $\hbar\to 0$ of Eq. (15). The Schrödinger equation for a single active electron in the Coulomb field of a system of point nuclear and electronic charges is given by

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2+V_{\text{ext}}(\mathbf{r})+\sum_{k=1}^{N-1}\frac{1}{|\mathbf{r}-\mathbf{r}_k|}-\lambda\right)\Psi(\mathbf{r};\{\mathbf{r}_k\})=0, \quad (32)$$

where the Lagrangian multiplier $\lambda$ is determined from the normalization condition

$$\int d^3\mathbf{r}\prod_{k=1}^{N-1}d^3\mathbf{r}_k|\Psi(\mathbf{r};\{\mathbf{r}_k\})|^2=1, \quad (33)$$

and we have suppressed spinor indices, by indicating their relevance if necessary. The examination of the classical limit of the Schrödinger equation (32) can be done by reintroducing the Planck constant $\hbar$. The limit $\hbar\to 0$ corresponds to large classical action for one electron, $S_0\gg\hbar$. The wave function for the active electron is written as [6]

$$\Psi(\mathbf{r};\{\mathbf{r}_k\})=e^{iS(\mathbf{r};\{\mathbf{r}_k\})/\hbar}. \quad (34)$$

By expanding the phase factor $S$ over the Planck constant $S=S_0+\hbar S_1+\hbar^2 S_2+\cdots$, in the leading order $\hbar^0$, the Schrödinger equation (32) simplifies to

$$[\nabla_{\mathbf{r}}S_0(\mathbf{r};\{\mathbf{r}_k\})]^2=2\left(\lambda-V_{\text{ext}}(\mathbf{r})-\sum_{k=1}^{N-1}\frac{1}{|\mathbf{r}-\mathbf{r}_k|}\right). \quad (35)$$

By introducing a positively defined and normalized to one distribution function for the spectator electrons

$$f(\mathbf{r}_1,\ldots\mathbf{r}_k,\ldots)=\int d^3\mathbf{r}\ e^{-2\ \text{Im}\ S_0(\mathbf{r};\{\mathbf{r}_k\})}, \quad (36)$$

and a complementary single-particle electron density

$$n(\mathbf{r})=\int\prod_{k=1}^{N-1}d^3\mathbf{r}_k\ e^{-2\ \text{Im}\ S_0(\mathbf{r};\{\mathbf{r}_k\})}, \quad (37)$$

normalized to the charge of one electron, $\int d^3\mathbf{r}\ n(\mathbf{r})=1$, multiplying Eq. (35) on the left by the distribution function, Eq. (36), and integrating over the variables of the spectators, we obtain the equation

$$p_F^2(\mathbf{r})=2\left[\lambda-V_{\text{ext}}(\mathbf{r})-(N-1)\int d^3\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right], \quad (38)$$

where we have introduced the unknown local Fermi momentum $p_F(\mathbf{r})$ by the equation

$$p_F^2(\mathbf{r})=\int\prod_{k=1}^{N-1}d^3\mathbf{r}_k(\nabla_{\mathbf{r}}S_0(\mathbf{r};\{\mathbf{r}_k\})^2\ f(\mathbf{r}_1,\ldots,\mathbf{r}_k,\ldots). \quad (39)$$

Equation (38) is a functional equation for the calculation of the unknown Lagrangian multiplier $\lambda$. Instead of using the exact (and yet unknown) statistical properties of the quasiclassical action $S_0$ provided by Pauli's exclusion principle, we employ the Thomas-Fermi approximation and the idea of occupied portion of the classical phase space for the fermions [6]. The electron density is expressed by the Fermi momentum as

$$n(\mathbf{r}) = 2\int \frac{d^3\mathbf{p}}{(2\pi)^3}\theta(p_F^2(\mathbf{r}) - p^2) = \frac{p_F^3(\mathbf{r})}{3\pi^2}. \tag{40}$$

By renormalizing the density in Eq. (37) to the total number of electrons, $N$, and substituting Eq. (40) into Eq. (38), we obtain the integral representation of the self-consistent Thomas-Fermi equation including the Amaldi correction:

$$(3\pi^2 n)^{2/3} = 2\left[\lambda - V_{\text{ext}}(\mathbf{r}) - \frac{N-1}{N}\int d^3\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]. \tag{41}$$

For atoms $N=Z$, the numerical solutions to the Thomas-Fermi-Amaldi equation are well documented in the literature—e.g., [6,7]. We just quote the characteristic properties of the solutions to these equations. The electron density $n(r)$ terminates abruptly for $r > r_0$, where $r_0$ is the classical turning point in the Thomas-Fermi-Amaldi potential $V_{\text{TFA}}(r)$ [cf. right-hand side of Eq. (41)]. The potential felt by a point electron at large distances $r \to \infty$ from the nucleus goes like $1/Nr$; i.e., it is a Coulomb potential with a strength equal to the inverse number of electrons in the atom. The Lagrangian multiplier $\lambda$ has the meaning of an ionization potential and does not vanish as in the original Thomas-Fermi equation, while it is given by $\lambda = V_{\text{TFA}}(r_0)$. A well-known drawback of the Thomas-Fermi and Thomas-Fermi-Amaldi equations when applied to molecules is the lack of binding, in accordance with the Teller's theorem [8].

## V. CONCLUSION

We have shown that the many-body Schrödinger equation for nonrelativistic system of $N$ electrons with Coulomb interactions exhibits a statistical reduction to three-dimensional Schrödinger equation for a single active electron with the surrounding $N-1$ electrons acting as spectators of its motion. The three-dimensional form of the Schrödinger spectator equations provides (i) a unified framework for the description of ground- and excited-state properties of the system and (ii) an interpretation of Pauli's exclusion principle as a dynamical principle that governs the electronic motions. We have examined the classical limit $\hbar \to 0$ of the given quantal equations; we provide an indication that these equations reduce to the Thomas-Fermi-Amaldi equation.

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