A Quantum Mechanics Conservation of Energy Equation for Stationary States with Real Valued Wave Functions

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Abstract

Many-body quantum-mechanical stationary states that have real valued wavefunction are shown to satisfy a classical conservation of energy equation with a kinetic energy function. The terms in the equation depend on the probability distribution, and, in addition, pressure and velocity functions, but these functions also depend on the probability distribution. There are two possible directions of the velocity that satisfy the energy equation. A linear momentum function is defined that integrates to zero, and this property is consistent with the expectation value of the linear momentum for stationary states with real-valued wave functions. The energy equation is integrated to obtain a version of the well known energy equation involving reduced density matrices, where the kinetic energy functional of the one-particle density matrix is replaced by a function of the electron density and a velocity function. Also, the noninteracting kinetic energy functional from the Hohenberg–Kohn theorem is given as an explicit functional of the orbital densities. For the purpose of describing the behavior of particles in a stationary state, a model based on the energy equation is constructed. The model is evaluated for the two different velocity directions using the grounds state of the particle in a one-dimensional box and the hydrogen atom. For one velocity direction, equations of motions with contradictory properties are obtained, and, in the other, an unstable system is found. A discussion is given with suggestions of additional elements that might improve the model.

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I. INTRODUCTION

There are some correspondence between classical-mechanical states with conservative potentials and stationary states of quantum mechanics. Both types of states satisfy an equation with the energy as a constant. For electronic systems, the external potential-energy and electron-electron repulsion energy functions for the time independent Schrödinger equation are obtained from classical mechanics, and they have a simple interpretation when the electrons are considered point masses with a negative charge. The correspondence for the kinetic energy is, for the most part, absent, if the particles are considered point masses with charge. The non-classical treatment of the kinetic energy also has consequences for density matrix theory \([1, 2]\), since the off diagonal elements of the one-particle density matrix, which seems to have no physical meaning and adds to the complexity of the problem, must be considered.

In this work, many-body quantum-mechanical stationary states that have real valued wavefunction are shown to satisfy a classical conservation of energy equation with a kinetic energy function (in Sec. II). The energy equation depends on the probability distribution, i.e., the square of the wavefunction, and pressure and velocity functions that also depend on the probability distribution, where there are two possible directions of velocity consistent with the energy equation.

A linear momentum function (in Appendix A) is defined that is consistent with the kinetic-energy function. As in the expectation value of the total momentum for quantum mechanical states with real-valued wave functions, the linear momentum function integrates (over all space and spin variables) to zero. This implies that the linear momentum function can be neither non-negative nor non-positive, if it is not the zero function.

In a manner that is consistent with the energy equation, a model that contains classical-mechanical elements is constructed (III) for the purpose of describing the behavior of particles in a stationary state. The model is evaluated for the two different velocity directions using the grounds state of the particle in a one-dimensional box and the hydrogen atom. For one velocity direction, equations of motions with contradictory properties are obtained, and, in the other, an unstable system is found that can only be stabilized by a nonclassical restriction on the velocity direction. These failures, however, may be useful in the path to the eventual formulation of a useful model of quantum mechanical states containing classical
mechanical elements that is based on the energy equation. For example, the construction of a more accurate model might be possible if the particles can frequently change velocity directions with no change in speed, or if a nonclassical restriction on the velocity direction is imposed, i.e., the particle only travels in the opposite direction of a force field.

The energy equation is integrated \[ (\text{IV}) \] to obtain a version of the well known energy equation \[ [2–4] \] involving reduced density matrices, where the kinetic energy functional of the one-particle density matrix is replaced by a function of the electron density and a velocity function. The final result is an equation that does not depend on the off diagonal elements of a reduced density matrix.

The noninteracting kinetic energy functional \( T_s \) from the Hohenberg–Kohn theorem \[ [2, 5] \] is given as an explicit functional of the orbital densities \( [V] \).

II. THE QUANTUM MECHANICS CONSERVATION OF ENERGY EQUATION FOR STATIONARY STATES

The \( n \)-body time-independent Schrödinger equation with a normalized, real-valued eigenfunction \( \psi \) can be written

\[
- \frac{\hbar^2}{2m} \sum_{i=1}^{n} \left[ \psi \nabla_i^2 \psi \right] + \sum_{i=1}^{n} v_i \gamma_n + \frac{1}{2} \sum_{i \neq j}^{n} r_{ij}^{-1} \gamma_n = \bar{E} \gamma_n
\]  

(1)

where

\[
\left[ \psi \nabla_i^2 \psi \right] (x) = \psi(x) \nabla_{r_i}^2 \psi(x), \quad x = x_1, \ldots, x_n
\]

Also, the \( n \)-body probability distribution \( \gamma_n \)—the diagonal part of the \( n \)-body density matrix—is \( \gamma_n = \psi^2 \); the electron coordinate \( x_i \) is defined by \( x_i = r_i, \omega_i \), where \( r_i \in \mathbb{R}^3 \) and \( \omega_i \in \{-1, 1\} \) are the spatial and spin coordinates, respectively. Furthermore, the \( v_i \) and \( r_{ij}^{-1} \) multiplicative operators are defined by the following:

\[
[v_i \gamma_n](x) = v(r_i) \gamma_n(x), \quad [r_{ij}^{-1} \gamma_n](x) = |r_i - r_j|^{-1} \gamma_n(x);
\]

where the one-body external potential \( v \) is a specified real-valued function with domain \( \mathbb{R}^3 \) such that \( \{ r \in \mathbb{R}^3 \mid \psi(x) = 0 \} \) has measure zero. This last requirements for \( v \) implies that the division of a equation by \( \psi \) or \( \gamma \) gives an equation that is defined almost everywhere. Henceforth, to reduce clutter, the \( n \) subscript appearing in the symbol \( \gamma_n \) is suppressed.
Substituting the following identity

\[-\frac{1}{2} \left[ \psi \nabla_i^2 \psi \right] = \frac{1}{8} \left[ \gamma^{-1} \nabla_i \gamma \cdot \nabla_i \gamma \right] - \frac{1}{4} \nabla_i^2 \gamma, \tag{2}\]

into the Schrödinger' (1), where the identity is easily derived \[\square\], gives

\[\frac{\hbar^2}{8m} \sum_{i=1}^{n} \gamma^{-1} |\nabla_i \gamma|^2 - \frac{\hbar^2}{4m} \sum_{i=1}^{n} \nabla_i^2 \gamma + \sum_{i=1}^{n} v_i \gamma + \frac{1}{2} \sum_{i \neq j}^{n} r_{ij}^{-1} \gamma = \bar{E} \gamma\]

Using the definitions

\[u_{i\pm} = \pm \frac{\hbar}{2m} \nabla_i \gamma, \quad p_i = -\frac{\hbar^2}{4m} \nabla_i^2 \gamma\] \tag{3}

and

\[\frac{1}{2} mu_i^2 = \frac{1}{2} m u_{i\pm} \cdot u_{i\pm} = \frac{1}{2} m \left| \frac{\hbar}{2m} \nabla_i \gamma \right|^2 = \frac{\hbar^2}{8m} \gamma^{-2} |\nabla_i \gamma|^2\]

we have

\[\sum_i \frac{1}{2} m \gamma u_i^2 + \sum_i p_i + \left( \sum_i v_i \right) \gamma + \left( \frac{1}{2} \sum_{i \neq j}^{n} r_{ij}^{-1} \right) \gamma = \bar{E} \gamma, \tag{4}\]

For any point \(x\) such that \(\gamma(x) \neq 0\), this equation can also be written

\[\sum_i \frac{1}{2} m \gamma u_i^2 + \left( \sum_i p_i \right) \gamma^{-1} + \sum_i v_i + \frac{1}{2} \sum_{i \neq j}^{n} r_{ij}^{-1} = \bar{E}\] \tag{5}

Another way to write it is

\[T + P \gamma^{-1} + V_{\text{nucl}} + V_{\text{ee}} = \bar{E}\] \tag{6}

where

\[T = \sum_i \frac{1}{2} m u_i^2, \quad P = \sum_i p_i, \quad V_{\text{nucl}} = \sum_i v_i, \quad V_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^{n} r_{ij}^{-1}\]

and where \(P\) is called the pressure and \(P \gamma^{-1}\) is called the compression energy, explicitly defined by

\[[P \gamma^{-1}](x) = \gamma^{-1}(x) \sum_i \left( -\frac{\hbar^2}{4m} \nabla_i^2 \gamma(r_i, \omega_1; \ldots; \gamma(r_n, \omega_n) \right)\]

Eq. (6) is a quantum-mechanical classical equation of the conservation of energy \(E\).

Next consider a one-body state, such that \(\psi(r, 1) = \phi(r) \alpha(1)\), where \(\alpha\) is the spin function that satisfies \(\alpha(1) = 1\) and \(\alpha(-1) = 0\). Hence, \(\gamma(r, 1) = \phi^2(r) \equiv \rho(r)\), and the last “equality” is a definition of the electron density \(\rho\). In this special case, \(\square\) and \(\square\) can be written

\[u_{i\pm} = \pm \frac{\hbar}{2m} \nabla \rho, \quad p = \frac{\hbar^2}{4m} \nabla^2 \rho\] \tag{7}

\[\frac{1}{2} mu^2 + p \rho^{-1} + v = \bar{E}\] \tag{8}
This last equation has been used to as a starting point to treat one-body steady-state quantum systems with real valued wave functions as fluids satisfying variants of well known equations from fluid dynamics, with body force \( v \), pressure \( p \), velocity field \( u \), and mass density \( m\rho \).

III. A MODEL CONSISTENT WITH THE ENERGY EQUATION (6)

Since we have an energy equation (6), a reasonable next step is the description of states of systems that satisfy specified constraints, such that (6) is satisfied. Another words, one or more models are needed. In this section, a model is given where the electrons are point masses with charge, and they behave like classical particles.

A. Components of a model

Let \((r, r + dr)\) denote a region of \(\mathbb{R}^3\), given by
\[
(r, r + dr) = (x, x + dx) \times (y, y + dy) \times (z, z + dz) \in \mathbb{R}^3
\]
where we use ‘1=’ for definitions. Let \(\gamma\) represent a stationary state such that the values of the spin variables and the locations of \(n\) electrons can be determined by experiment. The well known meaning given to \(\gamma\) is the following \([2–4]\): For a state represented by \(\gamma\), the real non-negative number
\[
\bar{\gamma} = n!\gamma(x) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n;
\]
is the probability of finding an electron (any one) in the volume element \((\mathbf{r}_1, \mathbf{r}_1 + d\mathbf{r}_1)\) with spin variable \(\omega_1\), an electron (a different one) in the volume element \((\mathbf{r}_2, \mathbf{r}_2 + d\mathbf{r}_2)\) with spin variable \(\omega_2\), \(\cdots\) and an electron (the last one) in the volume element \((\mathbf{r}_n, \mathbf{r}_n + d\mathbf{r}_n)\) with spin variable \(\omega_n\). In other words, it is the probability of finding the \(n\) electrons, in any order, in the following sequence of combined volume elements and spin variables: \((\mathbf{r}_1, \mathbf{r}_1 + d\mathbf{r}_1), \omega_1; (\mathbf{r}_2, \mathbf{r}_2 + d\mathbf{r}_2), \omega_2; \cdots (\mathbf{r}_n, \mathbf{r}_n + d\mathbf{r}_n), \omega_n\). Note that \(\bar{\gamma}\) is the value of a function at the point \(x\) and \(n\) regions of \(\mathbb{R}^3\) that is now specified.

Next we present a model that give interpretations for the functions from the previous section. First, however, a different meaning is given to \(\bar{\gamma}\), obtained by replacing the words 'the probability of finding' in the above interpretation with 'the fraction of time:'
I) The real non-negative number $\bar{\gamma}$ is the fraction of time the $n$ electrons, in any order, are contained in the following volume elements and have the following spin variables:

$$(r_1, r_1 + dr_1), \omega_1; (r_2, r_2 + dr_2), \omega_2; \cdots (r_n, r_n + dr_n), \omega_n.$$ 

Using interpretation I the following definition has a meaning without mentioning an experimental measurement:

**Definition.** An $n$-electron state is said to be at the spatial-spin location $x = \{r_1, \omega_1, \cdots r_1, \omega_1\}$ if there is an electron (any one) at the coordinate $r_1$ with spin variable $\omega_1$, an electron (a different one) at the coordinate $r_2$ with spin variable $\omega_2$, $\cdots$ and an electron (the last one) at the coordinate $r_n$ with spin variable $\omega_n$.

Next we give an interpretation to the energy terms in (6) and the pressure $P$.

Let the $n$-electron state be at the spatial-spin location $x$ such that $\gamma(x) \neq 0$.

IIa) The functions $T(x), [P\gamma^{-1}](x), V_{\text{nuc}}(r), V_{\text{ee}}(r)$ and $P(x)$ are the total values of the kinetic- $T$, compression- $P\gamma^{-1}$, external potential- $V_{\text{nuc}}$, and the electron-electron repulsion- $V_{\text{ee}}$ energies; and, $P(x)$ is the total value of the pressure.

Note that, all things being equal, the compression energy $P\gamma^{-1}$ is relatively large for spin-spatial locations $x$ that have a small fraction of time $\bar{\gamma}$.

Next we give an interpretation to individual functions that contribute to the energy terms in (6).

IIb) The function $v(r_i)$ is external potential for the electron located at $\{r_i, \omega_i\}$ from any spatial-spin location $x$ containing $\{r_i, \omega_i\}$. The function $r_{ij}^{-1}$ is the electron-electron repulsion energies between the electrons at $\{r_i, \omega_i\}$ and $\{r_j, \omega_j\}$ from any spatial-spin location $x$ containing $\{r_i, \omega_i\}$ and $\{r_j, \omega_j\}$. The functions $u_{\pm i}(x)$ and $p_{i}(x)$ are the velocity and pressure for the electron located at $\{r_i, \omega_i\}$ from the spatial-spin location $x$ that contains $\{r_i, \omega_i\}$, where there are two possible velocity directions, called uphill $u_{+i}$ and downhill $u_{-i}$ velocity.

B. Reservations and discussion

Interpretation IIb) might contradict the uncertainty principle for position and momentum, because when the $n$-electron state is at the spatial-spin location $x$, the momentum is
either $m\mathbf{u}_{+i}(\mathbf{x})$ or $m\mathbf{u}_{-i}(\mathbf{x})$ for the electron located at \{\textbf{r}_i, \omega_i\}.

For this paragraph, suppose IIb violates the uncertainty principle. This does not imply that a useful model to explain a class of phenomena cannot be constructed if it contains IIb, since useful models with flaws are common. One example is the assignment of orbital energies to a special class of orbitals that define a Slater single-determinantal wavefunction of Hartree–Fock theory. However, there exist other orbital sets that can define the same determinantal wavefunction, and these orbitals cannot be assigned orbital energies, at least not in the same way. Also, it is useful to have a simple starting point, where, later on, it might be possible to add corrections to treat this deficiency. For example, a Hartree product wavefunction does not provide an anti-symmetric wavefunction and distinguishes electrons, but it is an excellent starting point to introduce Slater-determinantal wavefunctions, since the individual terms of a Slater-determinant are Hartree products.

Let $\phi$ be a normalized wavefunction. Let $\chi$ be a normalized, nondegenerate eigenvector with eigenvalue $\lambda$ of a Hermitian operator $\hat{O}$ with a discrete spectrum representing an observable, such that the inner product $(\phi, \chi)$ of the $L^2$ Hilbert space satisfies $|\langle \phi, \chi \rangle|^2 \in (0, 1)$. Hence, $\phi$ and $\chi$ are linearly independent, but not orthogonal. According to an axiom of quantum mechanics [7, 8], if a measurement is made of the observable with operator $\hat{O}$ of the state represented by $\phi$, then the probability of the measured value being equal to $\lambda$ is $|\langle \chi, \phi \rangle|^2$. Also, if the measured value is $\lambda$, then the quantum mechanical system is in the state $\chi$ immediately after the measurement is made. In other words, the measurement has transformed the state $\phi$ into $\chi$. The same type of dramatic transformations are easily shown to hold for observers represented by bounded self-adjoint operators such that $\lambda$ corresponds to a degenerate subspace, and to cases where the operator $\hat{O}$ is unbounded, but still self-adjoint with a continuous spectrum. If it is possible to supplement the axioms of quantum mechanics by adding measurements that are not, in general, so destructive, but still provide information, then the interpretations above seem more reasonable. In a thought experiment it is easy to imagine the electron as having a specific position and momentum before a “measurement of destruction” is made, as in a position measurement that traps the electron in an infinitesimal three dimensional box.
C. Testing the model with velocity restrictions

Next, by applying (7) and (8) to two one-body states, we expose some problems with interpretations I and II, if the particle has a classical equation of motion that contains one and only one velocity function, that is, the single particle is described by either uphill $u_+$ and downhill $u_-$ velocity. We will also consider what additional restrictions or changes can be made to improve the situation. The calculations we do below have already been done for another purpose, where (7) and (8) are used to describe the fluid dynamics of one-body quantum states [6], where other one-body states are also treated.

1. Equations of motion with downhill velocity

For a particle in a one-dimensional box with a length that is 1 Bohr radius $a_0$, where the well known probability density in atomic units is $\rho(r) = 2 \sin^2(n\pi r)$ [9, 10], it is easily demonstrated that [6]

$$u_\pm(r) = \pm \frac{1}{2} \rho^{-1}(r) \frac{\partial \rho(r)}{\partial r} = \pm n\pi \cot(n\pi r), \quad n = 1, 2, \cdots$$

$$p(r) = -n^2 \pi^2 [1 - 2 \sin^2(n\pi r)]$$

for the two possible velocity directions, where $r \in [0, 1]$. Fig. 1 gives a classical energy diagram that also contains the downhill velocity $u_-$. Such diagrams of the potential and total energies are a familiar part of classical mechanics [11]. Since there is no external potential, the compression energy $p\rho^{-1}$ is the potential energy. Hence the distance between $\bar{E}_1$ and $p\rho^{-1}$ in the diagram is equal to the kinetic energy, as indicated by the energy equation (8). For the ground state ($n = 1$) the speed is zero at $r = 1/2$ and infinity at the nodes (at $r = 0, 1$). The point $r = 1/2$ is an unstable equilibrium point. A particle with downhill velocity $u_-$ at the point $r = 1/2 + \epsilon$, where $0 < \epsilon < 1/2$, will accelerate to the right and reach $r = 1$ in a finite amount of time, where the velocity is infinity, and where, according to interpretation I, the particle spends no time, since $r = 1$ is a node. Since, $u_-(0.5 - \epsilon) = -u_-(0.5 + \epsilon)$, the same behavior is exhibited for $r \in [0.1/2]$. Hence, a necessary condition for interpretations II to provide a useful model is that the particle must frequently change directions with constant speed, or transport—be destroyed at one point in space and simultaneously be created in another—and, if possible, do so in a way such
FIG. 1: The compression $p \rho^{-1}$ and total $\bar{E}_1$ energies with the probability density $\rho$ and downhill velocity $u_-$ of the ground-state of a particle in a one-dimensional box of length $a_0$ in atomic units from [6].

that interpretation I is satisfied.

For one electron atoms in the 1s state with atomic number $Z$ in spherical coordinates we have

$$\rho(r) = \frac{Z^3}{a_0^3} \pi^{-1} e^{-2Zr/a_0}, \quad u_+ = \mp \frac{Z \hbar m}{a_0} \hat{r},$$

where the density is well known [9, 10], and the velocity $u_\pm$ is computed using (7). (The pressure is examined in detail elsewhere for the hydrogen atom [6].) For $Z = 1$, $|u_\pm| = \hbar/ma_0$, and this is the speed of the electron in the first Bohr orbit of hydrogen [10]. Hence, the speed is constant and the electron is restricted to a single ray, or two opposite rays, if the electron can pass through the nucleus; the electron has zero angular momentum. For downhill velocity, the same necessary condition mentioned for the particle in a box is applicable for these states, except that the electron also must be able to change rays that are not on opposite sides of the nucleus.

**Conclusion #1.** The cost of violating the uncertainty principle is a particle that in a finite amount of time has infinite speed and is traveling nowhere, or one that does nothing more than travel towards an infinity.
Conclusion #2. According to Einstein “Everything should be made as simple as possible, but not simpler.” Perhaps the proposed model is too simple. In order for the above interpretations to be improved to give a satisfactory model, the interpretations must be modified or additional rules or variables must be added, and these variable(s) might need to be random. Also, since the states have pressure, it might be necessary for the electron to have a nonzero volume and be compressible.

2. Equations of motion with uphill velocity

For the particle in a box, if the particle is given an initial uphill velocity \( u_+ \) at a point \( r = 1/2 + \epsilon \), the particle moves in the direction of increasing electron density \( \rho \) until it becomes “perched” at \( r = 1/2 \) in an infinite amount of time, because the speed of the particle is zero at \( r = 1/2 \). However, stability is achieved at the point \( r = 1/2 \) only if the particle is restricted to uphill velocity \( u_+ \), so it cannot be ‘pushed off the top of the density hill,’ so to speak, at \( r = 1/2 \). This constraint does not have a classical correspondence.

For one electron atoms in the 1s state, there is a velocity discontinuity at the nucleus \( r = 0 \). It is difficult to see how this discontinuity can be consistent with an equation of motion for an electron described as a point-mass particle. However, if the external electrostatic potential is modified to take into account mass and volume effects of the nucleus, as in isotope shifts [10], then the external potential should have a minimum at the nucleus. Hence, the gradient of the electron density as \( r \to 0 \) is zero, giving a zero speed at the nucleus. This case is then modeled very well by the particle in a box, and with the same reservations.

Conclusion. Uphill velocity is only stable if the particle cannot have downhill velocity, and this restriction has no correspondence with classical states. The restriction implies that the particle only translates in the opposite direction of a force field.

IV. THE DENSITY MATRIX EQUATION WITHOUT OFF DIAGONAL ELEMENTS

Integrating (1) over all space and summing over all spin variables in atomic units, we obtain the well-known density-matrix energy equation [2–4]:

\[
\bar{E} = \frac{\hbar}{2m} \int \left[ \nabla^2 \rho_1(r, r') \right]_{r'=r} \, dr + \int v(r) \rho(r) \, dr + \int \int r_1^{-1} \rho_2(r_1, r_2) \, dr_1 \, dr_2 ; \tag{10}
\]
the one-body density matrix \( \rho_1 \) and pair function \( \rho_2 \) are defined by

\[
\rho_1(r_1, r'_1) = n \sum_{\omega_1 \cdots \omega_n} \int \psi(r_1, \omega_1, x_2, x_3, \cdots x_n) \psi(r'_1, \omega_1, x_2, x_3, \cdots x_n) \, dr_2 dr_3 \cdots dr_n,
\]

\[
\rho_2(r_1, r_2) = \frac{n(n-1)}{2} \sum_{\omega_1 \cdots \omega_n} \int \psi^2 \, dr_3 dr_4 \cdots dr_n,
\]

and the electron coordinate \( x_i \) is defined by \( x_i = r_i, \omega_i \), where \( r_i \) and \( \omega_i \) are the spatial and spin coordinates, respectively; the one-body density \( \rho \) is defined by \( \rho(r) = \rho_1(r, r) \).

Our objective is to integrate (4) over all space and sum over all spin coordinates and obtain an expression that resembles (10). Let \( r_i \) be a Cartesian coordinate, such that \( r_i = (x_i, y_i, z_i) \) and \( \alpha_i \in (x_i, y_i, z_i) \). We require that \( \psi \) satisfies the usual boundary conditions:

\[
\lim_{\alpha_i \to \infty} \psi(x) = \lim_{\alpha_i \to \infty} \frac{\partial \psi(x)}{\partial \alpha_i} = 0
\]

Using this requirement and \( \partial \gamma / \partial \alpha_i = 2 \psi (\partial \psi / \partial \alpha_i) \) we have

\[
\int_{-\infty}^{+\infty} \frac{\partial}{\partial \alpha_i} \left( \frac{\partial \gamma}{\partial \alpha_i} \right) \, d\alpha_i = 2 \left( \lim_{\alpha_i \to \infty} - \lim_{\alpha_i \to -\infty} \right) \psi \frac{\partial \psi}{\partial \alpha_i} = 0
\]

Using this identity and definition (3) it is easily proved that

\[
\int p_i(x) \, dr_i = 0
\]

Hence, the second term from (4) will not contribute after integrating over all space. Also, the pressure function \( p_i \) can be neither non-negative nor non-positive, if it is not the zero function.

Let the nonnegative function \( \tilde{u}_1^2 \) with domain \( \mathbb{R}^3 - \{ r \in \mathbb{R}^2 | \psi(r) = 0 \} \) be defined by

\[
\rho(r_1) \tilde{u}_1^2(r_1) = n \sum_{\omega_1 \cdots \omega_n} \int \gamma(s) u_1^2(s) \, dr_2 \cdots dr_n
\]

Using this definition, we treat the first term from (4):

\[
\frac{1}{2} \sum_i \sum_{\omega_1 \cdots \omega_n} \int m \gamma(s) u_i^2(s) \, dr_1 \cdots dr_n
\]

\[
= \frac{1}{2} n \sum_{\omega_1 \cdots \omega_n} \int m \gamma(s) u_1^2(s) \, dr_1 \cdots dr_n = \frac{1}{2} \int \rho_m(r_1) \tilde{u}_1^2(r_1) \, dr,
\]

where \( \rho_m = m \rho \). Using this result and the result above for the integration of the pressure term, we can integrate (4) over all space and sum over all spin coordinates to obtain our objective:

\[
E = \frac{1}{2} \int \rho_m(r) \tilde{u}^2(r) \, dr + \int v(r) \rho(r) \, dr + \int \int r_{12}^{-1} \rho_2(r_1, r_2) \, dr_1 \, dr_2 \quad (11)
\]
The classical electrostatic interpretation of the second term is that it is the electrostatic energy assigned to the charge density $q\rho$, also called a charge cloud, where $q$ is the charge of the indistinguishable particles. Similarly, the first term is the kinetic energy of the mass density or “mass cloud,” a continuum in motion, i.e., a fluid, where $\rho_m(r)$ and $|\vec{u}(r)|$ are the average mass density and speed at $r$, respectively.

V. THE KINETIC ENERGY FUNCTIONAL OF THE HOHENBERG–KOHN THEOREM OF NONINTERACTING ELECTRONS

Equation (2), in the fictitious case of a single electron without spin, is

$$-\frac{1}{2} \phi \nabla^2 \phi = 1 \frac{1}{8} \rho^{-1} \nabla \rho \cdot \nabla \rho - \frac{1}{4} \nabla^2 \rho,$$

where $\rho = \phi^2$, and this equation also holds for a case where a value of the spin variable is taken, as in (7) and (8). Using this equation, the kinetic energy functional $K_s$ from the Hohenberg–Kohn theorem \[2, 5\] for the special case of one-electron states with a non-degenerate wavefunction $\psi$ is, explicitly given by

$$K_s[\rho] = -\frac{\hbar^2}{2m} \int_{\mathbb{R}^3} \phi \nabla^2 \phi \, dr = \frac{\hbar^2}{m} \int_{\mathbb{R}^3} \left( \frac{1}{8} \rho^{-1} \nabla \rho \cdot \nabla \rho - \frac{1}{4} \nabla^2 \rho \right) \, dr,$$

and note that any non-degenerate ground state can be represented by a real valued eigenfunction. Eq. (12) is an equality, not an identity, that holds for the set of all one-electron stationary states such that $\rho$ is either the electron density of a nondegenerate ground-state or a degenerate state that has a real-valued eigenfunction.

Consider a ground state of $N$ noninteracting electrons, with spin not included, and with the Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i, \quad \hat{h}_i = -\frac{1}{2} \nabla^2 \phi_i(r_i) + v_s(r),$$

where the ground-state eigenfunction is a real-valued Slater determinant constructed from $N$ real-valued, orthonormal, spatial-orbitals $\{\phi_1, \cdots \phi_N\}$. Using (12), the well know noninteracting kinetic energy functional $T_s$ from the Hohenberg–Kohn theorem \[2, 5\] is given as an explicit functional of the orbital densities $\rho_i = \phi_i^2$:

$$T_s[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \int_{\mathbb{R}^3} \phi_i \nabla^2 \phi_i \, dr = \sum_{i=1}^{N} K_s[\rho_i]; \quad \rho = \sum_{i=1}^{N} \rho_i,$$

and this functional is a key component of the Kohn–Sham methodology of density functional theory \[2, 5\].
Appendix A: The linear momentum vector function

In this section a total linear momentum function is defined that integrates over all space to zero, and this property is consistent with the expectation value of the linear momentum for stationary states with real-valued wave functions.

For any functions $Y = Y(x)$ such that $\gamma \mapsto Y$, i.e., $\gamma$ determines $Y$, let $\langle Y \rangle_\gamma$ be defined by

$$\langle Y \rangle_\gamma = \sum_{\omega_1 \cdots \omega_n} \int Y(x) \, d\mathbf{r}_1 \cdots d\mathbf{r}_n$$

where $\gamma = \phi^2$ and $\phi = \phi(x)$ is a real-valued function that is a member of the $L^2$ Hilbert space.

Let $I_R$ be an index set of three symbols, given by $I_R = \{x, y, z\}$. Let $\hat{L}_\alpha$ denote the $\alpha$ component of the total linear momentum operator $\hat{L}$, i.e.,

$$\hat{L}_\alpha = \sum_{j=1}^{n} i\hbar \frac{\partial}{\partial \alpha_j}, \quad \alpha \in I_R$$

Since, $\alpha_j \partial \phi / \partial \alpha_j$ is real, the expectation value $\langle \phi | \hat{L}_\alpha | \phi \rangle$ is pure imaginary or zero. Since $\hat{L}_\alpha$ is Hermitian, any expectation value must be real. Hence, using Dirac notation

$$\langle \phi | \hat{L}_\alpha | \phi \rangle = 0. \quad (A1)$$

Let the total linear-momentum vector-function $\mathbf{\bar{P}}_\pm$ be defined by

$$\mathbf{\bar{P}}_\pm = \sum_{i=1}^{n} m \mathbf{u}_i \pm$$

Let $m \mathbf{u}_{\alpha, \pm}$ denote the $\alpha \in (x, y, z)$ Cartesian component of $m \mathbf{u}_{\pm}$, i.e.,

$$m \mathbf{u}_{\alpha, \pm} = (m \mathbf{u}_\pm) \cdot \mathbf{\hat{e}}_\alpha = \pm \frac{\hbar}{2} \gamma^{-1} \frac{\partial \gamma}{\partial \alpha_i} = \pm \frac{\hbar}{2} \frac{\partial (\ln \gamma)}{\partial \alpha_i},$$

where (3) is used, and so that $\ln \gamma$ is defined, we use atomic units. Using the resolution of the identity, $\mathbf{\bar{P}}_\pm$ can be resolved into components

$$\mathbf{\bar{P}}_\pm = \sum_{i=1}^{n} \sum_{\alpha \in I_R} [(m \mathbf{u}_\pm) \cdot \mathbf{\hat{e}}_\alpha] \mathbf{\hat{e}}_\alpha = \sum_{i=1}^{n} \sum_{\alpha \in I_R} m \mathbf{u}_{\alpha, \pm} \mathbf{\hat{e}}_\alpha$$

Hence $\gamma \mapsto \mathbf{\bar{P}}_\pm$. From

$$\int_{-\infty}^{+\infty} m \mathbf{u}_{\alpha, \pm}(x) \, d\alpha_i = \pm \frac{\hbar}{2} \left( \lim_{\alpha_i \to +\infty} \ln \gamma(x) - \lim_{\alpha_i \to -\infty} \ln \gamma(x) \right) = 0$$
it follows that
\[
\langle m\alpha_{i\pm}\rangle_\gamma = \sum_{\omega_1\cdots\omega_n} \int m\alpha_{i\pm}(x) \, dr_1 \cdots dr_1 = 0
\]
Hence
\[
\langle \phi|\hat{L}|\phi \rangle = \langle \hat{P}_\pm \rangle_\gamma = 0, \quad \gamma = \phi^2
\]
where (A1) is used and
\[
\hat{L} = \sum_{\alpha \in I_R} \hat{L}_\alpha \hat{e}_\alpha
\]
is the total linear momentum operator.

The equality \( \langle \hat{P}_\pm \rangle_\gamma = 0 \) implies that the momentum function can be neither non-negative nor non-positive, if it is not the zero function, and it is consistent with \( \langle \phi|\hat{L}|\phi \rangle = 0 \), the average value of the momentum.

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