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REGULAR ARTICLE

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Density bifunctional theory using the mass density and the charge density

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Abstract Can all the properties of a system composed of particles with masses, m_i, and charges, q_i, be determined from the charge density and the mass density? Subject to a small statistical caveat, this is true, and offers the prospect of an elegant extension of density-functional theory beyond the Born-Oppenheimer approximation.

Keywords Density functional theory · Mass density · Born–Oppenheimer approximation

1 Introduction

Consider a system composed of p distinct types of elementary particles, which are presumed to interact only via electrostatic and gravitational forces. Neglecting relativity, the Hamiltonian has the form [1]:

$$\hat{H} = \sum_{\alpha=1}^{p}\sum_{i=1}^{N_\alpha}\left(-\tfrac{\nabla^2_{\alpha i}}{2m_\alpha} + v\left(\mathbf{r}_{\alpha i}\right)\right) + \frac{1}{2}\sum_{\alpha=1}^{p}\sum_{\beta=\alpha}^{p}\sum_{i=1}^{N_\alpha}\sum_{j=i}^{N_\beta}(1-\delta_{\alpha\beta}\delta_{ij})\left(\tfrac{q_\alpha q_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|} - \tfrac{m_\alpha m_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|}\right) \quad (1)$$

where $v(\mathbf{r}_{\alpha i})$ is the external potential that confines the N_α particles of type α. The Hohenberg-Kohn theorem applies to the case where there is only one type of particle in the system—say, electrons. In this case, the density of particles determines all the properties of the system. One often states that, unlike the wave function, the density of particles is experimentally observable. However, what one really observes via photon (X-ray) or neutron scattering is the charge density,

$$\rho^{(e)}(\mathbf{x}) \equiv \Big\langle \Psi\left(\mathbf{r}_{11},\ldots,\mathbf{r}_{1N_1},\mathbf{r}_{21},\ldots,\mathbf{r}_{2N_2},\mathbf{r}_{31},\ldots\mathbf{r}_{pN_p}\right)\Big| \times \sum_{\alpha=1}^{p}\sum_{i=1}^{N_p} q_\alpha\delta\left(\mathbf{r}_{\alpha i}-\mathbf{x}\right) \times \Big|\Psi\left(\mathbf{r}_{11},\ldots,\mathbf{r}_{1N_1},\mathbf{r}_{21},\ldots\mathbf{r}_{pN_p}\right)\Big\rangle, \quad (2)$$

or mass density,

$$\rho^{(m)}(\mathbf{x}) \equiv \Big\langle \Psi\left(\mathbf{r}_{11},\ldots,\mathbf{r}_{1N_1},\mathbf{r}_{21},\ldots,\mathbf{r}_{2N_2},\mathbf{r}_{31},\ldots\mathbf{r}_{pN_p}\right)\Big| \times \sum_{\alpha=1}^{p}\sum_{i=1}^{N_p} m_\alpha\delta\left(\mathbf{r}_{\alpha i}-\mathbf{x}\right) \times \Big|\Psi\left(\mathbf{r}_{11},\ldots,\mathbf{r}_{1N_1},\mathbf{r}_{21},\ldots\mathbf{r}_{pN_p}\right)\Big\rangle. \quad (3)$$

When there is only one type of particle, both the charge density and the mass density are directly proportional to the particle density.

The extension of the Hohenberg–Kohn theorem to systems composed of many different types of particles was first considered by Capitani et al. [1] who showed that if you know the particle densities of each different type of particle, $\{\rho_\alpha(\mathbf{r})\}_{\alpha=1}^{p}$, then all properties of the system are determined. [2] However, densities of the particles composing the system are usually not experimentally observable. (Constructing the particle densities for a p-component system requires one to find p experimental "probe particles," each of which interacts in a distinct way with the particle types that compose the system.)

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Is it possible to determine the properties of the system from the charge density and mass density alone? This is usually the case. To see this, consider the following extension of the Hohenberg–Kohn Theorem [2]:

Lemma *Consider a system composed of p distinct types of particles. Suppose that the number of each type of particle, along with the masses and charges of the particles, is known. Then all properties of the system can be determined from the mass and charge density.*

Proof If the mass, charge, and cardinality of each distinct type of particles is known, then we can be sure that the Hamiltonian has the form of Eq. 1, where only the external potentials are unknown. If, as assumed here, the particles interact only via gravitational and electrostatic forces, the external potential will be due to fields of these types also, and so the energy of the system can be written as:

$$\begin{aligned}
&E_{v^{(e)},v^{(m)}}\left[\Psi\right] \\
&\quad= \left\langle \Psi \middle| \left\{ \sum_{\alpha=1}^{p} \sum_{i=1}^{N_\alpha} -\tfrac{\nabla_{\alpha i}^2}{2m_\alpha} \right.\right. \\
&\qquad \left. + \frac{1}{2} \sum_{\alpha=1}^{p} \sum_{\beta=\alpha}^{p} \sum_{i=1}^{N_\alpha} \sum_{j=i}^{N_\beta} (1-\delta_{\alpha\beta}\delta_{ij}) \left(\tfrac{q_\alpha q_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|} - \tfrac{m_\alpha m_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|} \right) \right\} \\
&\qquad \times \left| \Psi \right\rangle \\
&\qquad + \int \rho^{(m)}\left(\mathbf{r}\right) v^{(m)}\left(\mathbf{r}\right) \mathrm{d}\mathbf{r} + + \int \rho^{(e)}\left(\mathbf{r}\right) v^{(e)}\left(\mathbf{r}\right) \mathrm{d}\mathbf{r}. \qquad (4)
\end{aligned}$$

where $-\nabla v^{(m)}(\mathbf{r})$ and $-\nabla v^{(e)}(\mathbf{r})$ are the external gravitational and electric fields, respectively. Consider a second choice for the external potentials, $\tilde{v}^{(m)}(\mathbf{r})$ and $\tilde{v}^{(e)}(\mathbf{r})$, and denote the ground-state wave function and densities for these potentials as $\tilde{\Psi}$, $\tilde{\rho}^{(m)}(\mathbf{r})$, and $\tilde{\rho}^{(e)}(\mathbf{r})$. From the variational principle for the energy, one has that

$$\begin{aligned}
&\left\langle \Psi \middle| \hat{F} \middle| \Psi \right\rangle + \textstyle\int \rho^{(m)}(\mathbf{r}) v^{(m)}(\mathbf{r}) \mathrm{d}\mathbf{r} + \textstyle\int \rho^{(e)}(\mathbf{r}) v^{(e)}(\mathbf{r}) d\mathbf{r} \\
&\quad < \left\langle \tilde{\Psi} \middle| \hat{F} \middle| \tilde{\Psi} \right\rangle + \textstyle\int \tilde{\rho}^{(m)}(\mathbf{r}) v^{(m)}(\mathbf{r}) \mathrm{d}\mathbf{r} + \textstyle\int \tilde{\rho}^{(e)}(\mathbf{r}) v^{(e)}(\mathbf{r}) \mathrm{d}\mathbf{r} \\
&\left\langle \tilde{\Psi} \middle| \hat{F} \middle| \tilde{\Psi} \right\rangle + \textstyle\int \tilde{\rho}^{(m)}(\mathbf{r}) \tilde{v}^{(m)}(\mathbf{r}) \mathrm{d}\mathbf{r} + \textstyle\int \tilde{\rho}^{(e)}(\mathbf{r}) \tilde{v}^{(e)}(\mathbf{r}) d\mathbf{r} \\
&\quad < \left\langle \Psi \middle| \hat{F} \middle| \Psi \right\rangle + \textstyle\int \rho^{(m)}(\mathbf{r}) \tilde{v}^{(m)}(\mathbf{r}) \mathrm{d}\mathbf{r} + \textstyle\int \rho^{(e)}(\mathbf{r}) \tilde{v}^{(e)}(\mathbf{r}) \mathrm{d}\mathbf{r}
\end{aligned} \qquad (5)$$

where we have defined, in analogy to the usual definition of the Hohenberg–Kohn functional,

$$\begin{aligned}
\hat{F} \equiv& \sum_{\alpha=1}^{p} \sum_{i=1}^{N_\alpha} -\tfrac{\nabla_{\alpha i}^2}{2m_\alpha} \\
&+ \sum_{\alpha=1}^{p} \sum_{\beta=\alpha}^{p} \sum_{i=1}^{N_\alpha} \sum_{j=i}^{N_\beta} (1-\delta_{\alpha\beta}\delta_{ij}) \left(\tfrac{q_\alpha q_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|} - \tfrac{m_\alpha m_\beta}{\left|\mathbf{r}_{\alpha i}-\mathbf{r}_{\beta j}\right|} \right). \qquad (6)
\end{aligned}$$

In using a strict inequality for Eq. (5), it is assumed that the external fields of the two systems are not the same, which requires that the external potentials differ by more than an additive constant.

Adding Eqs. (5) together yields

$$\begin{aligned}
&\int \left(\rho^{(m)}\left(\mathbf{r}\right) - \tilde{\rho}^{(m)}\left(\mathbf{r}\right)\right) \left(v^{(m)}\left(\mathbf{r}\right) - \tilde{v}^{(m)}\left(\mathbf{r}\right)\right) \mathrm{d}\mathbf{r} \\
&\quad + \int \left(\rho^{(e)}\left(\mathbf{r}\right) - \tilde{\rho}^{(e)}\left(\mathbf{r}\right)\right) \left(v^{(e)}\left(\mathbf{r}\right) - \tilde{v}^{(e)}\left(\mathbf{r}\right)\right) \mathrm{d}\mathbf{r} < 0 \qquad (7)
\end{aligned}$$

Equation (7) cannot hold if $\rho^{(m)}\left(\mathbf{r}\right) = \tilde{\rho}^{(m)}\left(\mathbf{r}\right)$ and $\rho^{(e)}\left(\mathbf{r}\right) = \tilde{\rho}^{(e)}\left(\mathbf{r}\right)$, implying that systems with different external electric and gravitational fields always have different mass and charge densities. Consequently, the electric and gravitational field are functionals of the mass and charge densities. This allows one to determine the electrostatic and gravitational potentials (to within an immaterial additive constant), yielding the Hamiltonian, Eq. (1). The Schrödinger equation can then be solved and all properties of the system (e.g., the energy—cf. Eq. (4)) can be determined. □

It remains to be shown that the identity (which determines the characteristic masses and charges) and number of particles in the system can be determined from the charge density and the mass density. To clarify the situation, consider the case where there are only two different types of particles. By integrating the mass density one can find the total mass of the system, giving the equation

$$N_1 m_1 + N_2 m_2 = m_{\text{total}} = \int \rho^{(m)}\left(\mathbf{r}\right) \mathrm{d}\mathbf{r}. \qquad (8)$$

Suppose this equation has two solutions; then

$$\begin{aligned}
&(N_1 - n_1)\, m_1 + (N_2 - n_2)\, m_2 = 0 \\
&\qquad \frac{N_1 - n_1}{N_2 - n_2} = -\frac{m_2}{m_1}. \qquad (9)
\end{aligned}$$

The left-hand side of Eq. (9) is necessarily a rational number. If we presume, however, that the masses of elementary particles are taken "at random" from the positive real numbers, the right-hand-side of Eq. (9) is, with probability one, an irrational number. (There are infinitely more irrational numbers than rational numbers, which is obvious from the fact that the set of rational numbers is countable, while the union of the set of rational and irrational numbers (the set of real numbers) is not. From a different perspective, since each successive digit in the mass of a particle should be independent of those that came before, it is infinitely unlikely that the mass of a given particle will be a repeating decimal. Rational numbers are always representable as repeating decimals.)

Thus, with probability one, Eq. (8) has but one solution. This is not to say that this is the case in numerical work. Given the finite experimental precision with which the masses of elementary particles and nuclides are known, in practical work the masses and ratios of masses of the particles will always be rational. However, for small systems, the left-hand-side of Eq. (9) will be a fraction with a small denominator, whilst the right-hand-side will, with high probability, not be reducible to a fraction with a small denominator.

The extension of this argument to more than two types of particles is straightforward; specifically, one desires that the equation

$$\sum_{i=1}^{p}(N_i - n_i)\,m_i = 0, \tag{10}$$

where N_i and n_i are restricted to be nonnegative integers, to have only one solution (with $N_i = n_i$ for all i). (In Eq. (10), p is the total number of particles under consideration; for chemical purposes this set likely consists of common nuclides, electrons, and perhaps—if one is interested in exotic matter—a few of the more stable elementary particles.) Statistically speaking, each of these masses would be an irrational number. To investigate solutions to Eq. (10), it is useful to restate the equation as the vector equation,

$$\mathbf{d} \cdot \mathbf{m} = 0 \tag{11}$$

where the elements of **m** are the masses of the particles in question. If **m** is a p-dimensional vector, there will be a $(p-1)$-dimensional subspace that solves Eq. (11). We need to investigate whether there any integer vectors in this subspace and, if so, whether $\mathbf{N} = \mathbf{n} \pm \mathbf{d} \geqslant 0$. Denote basis vectors of the orthogonal subspace as (that is, the basis set for the vectors that satisfy $\mathbf{d} \cdot \mathbf{m} = 0$) as $\{\mathbf{b}_i\}_{i=1}^{p-1}$. Since the elements of the basis vectors are normalized linear combinations of the particle masses, they are also usually irrational numbers. Equation (11) becomes equivalent to the question of whether one can find numbers, k_i, such that the vector $\sum\limits_{i=1}^{p-1} k_i \mathbf{b}_i$ is a vector of nonnegative integers. While equations of this type can have solutions, the probability that it has a solution is zero. Thus, with probability one, knowing the mass density of a system determines the identity and quantity of particles that compose the system. Referring to the lemma, it follows that, with probability one, the charge density and mass density determine all properties of a system.

There are, of course, vectors of integers, **d**, that *almost* solve Eq. (11). For example, there will be solutions with $\mathbf{d} \cdot \mathbf{m} \leqslant 10^{-9}$. Since particles' masses are only known to finite precision, any solution that has smaller error than the error in the input masses should be accepted. In practice, many nuclide masses are known to a precision of about $10^{-9}\mathbf{u}$, so $\mathbf{d} \cdot \mathbf{m} \leqslant 10^{-9}$ is often a reasonable standard. For systems with only a few nuclei, however, the magnitude of the solution vector tends to be about $|\mathbf{d}| = 10^9$, which gives patently absurd choices for the numbers of nuclei.

This is best illustrated by an example. Consider isotope-labeled ethanol, $^{14}_{6}\mathrm{CH}_3 - {}^{12}_{6}\mathrm{CD}_2\mathrm{OH}$. In this system we have 26 electrons ($m = 5.485799095 \cdot 10^{-4}$u), one Carbon-14 nucleus ($m = 14.003241988$ u), one Carbon-12 nucleus (12.000000000u), four protons ($m = 1.0078250321$ u), two deuterium nuclei ($m = 2.0141017779$ u), and one Oxygen-16 nucleus ($m = 15.9949146196$ u). Presume, for simplicity, that we know the types of nuclei but not the number of nuclei, then the mass vector has only 6 terms, and is given by [4,5]

$$\mathbf{m} = \begin{bmatrix} m_e & m_{^1_1\mathrm{H}} & m_{^2_1\mathrm{H}} & m_{^{12}_6\mathrm{C}} & m_{^{14}_6\mathrm{C}} & m_{^{16}_6\mathrm{O}} \end{bmatrix}^T. \tag{12}$$

We now need to study solutions to Eq. (11), subject to the caveat that **d** is a vector of integers. Moreover, since the number of particles of each type should be positive, the sum of the known solution, $\mathbf{n} = \begin{bmatrix} 26\ 4\ 2\ 1\ 1\ 1 \end{bmatrix}^T$, and $\pm\mathbf{d}$ should be positive. Since there are only six different masses in this problem, there is a five-dimensional vector space of solutions to Eq. (11). Because **m** is a vector of rational numbers (owing to the finite precision of the experimental measurement), there will be elements of this vector space with integer coefficients, but it is unlikely that these coefficients will be small. As a rough guess, the typical size of the integer coefficients will reflect the precision of the experimental masses, so with masses accurate to a 10^{-9}u, we expect for nontrivial integer solutions to Eq. (11) to feature ridiculously large numbers—on the order of 10^8.

Numerical solution of the equation (11) found no reasonable nontrivial solutions. Solutions do exist, but among the elements of **d** is a large negative integer, which is inconsistent with the fact that the alternative assignment of nuclei to the molecule (given by $\mathbf{n} \pm \mathbf{d}$) is nonnegative. Among the solutions located, the one with the smallest magnitude was $\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 3{,}500{,}810{,}497 & -3,000,000,000 & 0 \end{bmatrix}^T$, but this clearly does not refer to a "real" solution, since a molecule cannot have a negative number of atoms of any isotope. If the numerical precision of the nuclide masses were smaller, however, then the size of the elements of **d** would also be smaller and, perhaps, more reasonable. By contrast, in the hypothetical limit of infinite precision measurements we expect that the magnitude of **d** will tend toward infinity, so that there is no feasible solution.

It is important to note that it is usually impermissible to have both particles and antiparticles in one's system: since a particle and its antiparticle have the same mass, one cannot determine the partitioning between antiparticles and particles from the total mass alone. However, since a particle and its antiparticle annihilate, giving photons, this may be viewed as an "excited state;" consequently, this limitation is just a generalization of the usual caveat that density-functional theory is a theory of ground states. The inability to treat particle-antiparticle pairs is also unproblematic since, in general, such interactions should be treated in a relativistic framework.

Though treating nuclear forces in the context of non-relativistic quantum mechanics is very questionable, if one does so–introducing the "color charge" density, $\rho^{(c)}(\mathbf{r})$, and the "weak charge" density, $\rho^{(w)}(\mathbf{r})$, to model the strong and weak nuclear forces, respectively, then one obtains an attractively symmetric theory with four fundamental densities (corresponding to the four fundamental forces) in four dimensions (three spatial dimensions plus time).

Aside from its conceptual interest, this result may have computational potential. The original result of Capitani, Nalewajski, and Parr was proposed to develop a "non-Born-Oppenheimer" density-functional theory. [2] For this application, the number and types of nuclei under consideration is usually small and, moreover, known. (Often, in fact, one would treat only the light nuclei quantum mechanically, lumping the effects of heavier atoms into the external potentials.)

With identity and quantity of particles known, it follows from the lemma (there is no need for the probabilistic argument) that the charge and mass densities determine everything about the system, and the resulting theory certainly has a simpler structure (it is a bifunctional theory, rather than a p-functional theory) than the result of Capitani et al.. [2] In addition, if one is primarily interested in the electronic properties of the system, an important effect is the "smearing" of the positive charges on the nuclei, which is directly discernable from the mass and charge densities. In fact, one can determine "nuclear" and "electron" densities directly from the mass and charge densities using the equations

$$\begin{gathered}(-e)\,\rho^{(\text{electron})}(\mathbf{r})+\left(e\sum_{i=1}^{p-1}N_iZ_i\right)\sigma^{(\text{nuclear})}(\mathbf{r})=\rho^{(e)}(\mathbf{r})\\(m_e)\,\rho^{(\text{electron})}(\mathbf{r})+\left(\sum_{i=1}^{p-1}N_im_i\right)\sigma^{(\text{nuclear})}(\mathbf{r})=\rho^{(m)}(\mathbf{r})\,.\end{gathered}\tag{13}$$

Here, the electron is considered to be the pth type of particle, and so the pth term in the summations is omitted. Using Eq. (13), the charge density and mass density of each atomic nucleus can be determined by multiplying the total nuclear charge or total nuclear mass by the nuclear "shape function," $\sigma^{(\text{nuclear})}(\mathbf{r})$.

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References

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