

Direct first principles algorithm for the universal electron density functional

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Citation: *J. Chem. Phys.* **77**, 396 (1982); doi: 10.1063/1.443619

View online: <https://doi.org/10.1063/1.443619>

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Direct first principles algorithm for the universal electron density functional

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An explicit formula is provided giving a formal derivation of the exact universal electron density functional. This abstract theorem enables the derivation of a functional Taylor series expansion of this density functional about a reference density. Although wave function methods are used in the derivation, the final quantities may be evaluated by a variety of methods including nonwave function many-body methods.

The Hohenberg-Kohn (HK) theorem proves that there exists a unique universal functional $F[\rho]$ of the electron density $\rho(\mathbf{r})$ such that

$$E_v[\rho] \equiv \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[\rho] \quad (1)$$

is always an upper bound ($E_v[\rho] \geq E$) to the true ground state energy E for the system with the local "external" (i.e., electron-nuclear) potential $v(\mathbf{r})$. Hence, in principle, the calculation of ground state energies requires only a knowledge of the universal functional $F[\rho]$ and v , since the minimization of $E_v[\rho]$ produces the ground state energy and density.¹⁻⁷

Because of the apparent circumvention of the need for considering N -electron wave functions, considerable interest has focused upon the determination of an exact and explicit form for $E_v[\rho]$ which is amenable to *ab initio* calculations to any desired accuracy. Note that $E_v[\rho]$ as a functional is merely a rule for associating a single number $E_v[\rho]$ with the full function $\rho(\mathbf{r})$. Here we first provide an abstract theorem giving a derivation of the exact $E_v[\rho]$. Following the statement and proof of the theorem, this abstract representation is used to provide an explicit formula for the exact $E_v[\rho]$ as a Taylor expansion in powers of the difference between $\rho(\mathbf{r})$ and a reference density $\rho_0(\mathbf{r})$. The coefficients in this expansion may directly be calculated by a variety of different *ab initio* methods which consider the response of the N -electron system to a weak external field, thereby providing the *first rigorous* means for direct calculation of $E_v[\rho]$. Although wave function based arguments are provided in the derivation, the essential quantities may be calculated by nonwave function methods such as those provided by many-body theory. Hohenberg and Kohn¹ provide an expansion for the case of uniform density; we derive the generalization for arbitrary nonuniform systems.

We begin with a physical motivation of the general results. $E_v[\rho]$ may be interpreted as the ground state energy of the system with external potential $v(\mathbf{r})$ if the density were $\rho(\mathbf{r})$. But the ground state density is actually $\rho_0(\mathbf{r})$. Then how can we convert the system with $v(\mathbf{r})$ and $\rho_0(\mathbf{r})$ to the density $\rho(\mathbf{r})$ in order to evaluate the

energy $E_v[\rho]$? This can be accomplished by applying an additional external "driving" potential $\Lambda(\mathbf{r})$ to shift the density from $\rho_0(\mathbf{r})$ to $\rho(\mathbf{r})$. The HK theorem shows¹ that $v(\mathbf{r}) + \Lambda(\mathbf{r})$ is a unique functional of $\rho(\mathbf{r})$. So, in principle, it is possible to invert this relation to determine the $\Lambda(\mathbf{r})$ necessary to produce $\rho(\mathbf{r})$. An example of this inversion procedure is given below.

For notational simplicity we consider the quantity $E_v[\rho]$ containing v . The theorem defining the calculation of the exact $E_v[\rho]$ is as follows: Let H be the N -electron Hamiltonian with v present. Further let

$$\Lambda = \sum_{i=1}^N \lambda(\mathbf{r}_i) = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) \lambda(\mathbf{r}), \quad (2)$$

with $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$, be the "driving" potential. Compute the ground state wave function $\psi_\Lambda[\lambda]$ corresponding to $H + \Lambda$. The associated ground state energy is

$$E_\Lambda[\lambda] = \langle \psi_\Lambda[\lambda] | H + \Lambda | \psi_\Lambda[\lambda] \rangle / \langle \psi_\Lambda[\lambda] | \psi_\Lambda[\lambda] \rangle, \quad (3)$$

while the normalized ground state density with $\int d\mathbf{r} \rho(\mathbf{r}) = N$ is

$$\rho(\mathbf{r}; [\lambda]) = \langle \psi_\Lambda[\lambda] | \hat{\rho}(\mathbf{r}) | \psi_\Lambda[\lambda] \rangle / \langle \psi_\Lambda[\lambda] | \psi_\Lambda[\lambda] \rangle. \quad (4)$$

In Eq. (4), the value of $\rho(\mathbf{r})$ on the left depends on the whole function $\lambda(\mathbf{r})$ on the right; hence, the functional notation $\rho(\mathbf{r}; [\lambda])$. Inversion of Eq. (4) (because of the HK theorem) gives the $\lambda(\mathbf{r})$ necessary to produce a chosen $\rho(\mathbf{r})$, i.e., gives $\lambda(\mathbf{r}; [\rho])$. With this inversion, derived below, Eqs. (3) and (4) represent the HK density functional $E_v[\rho]$ as the Legendre transformation of $E_\Lambda[\lambda]$,

$$E_v[\rho] = E_\Lambda[\lambda] - \int d\mathbf{r} \rho(\mathbf{r}) \lambda(\mathbf{r}), \quad (5)$$

where as derived below we have²

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = -\lambda(\mathbf{r}; [\rho]), \quad (6)$$

and the relation $\lambda = \lambda(\mathbf{r}; [\rho])$ is used in the right-hand side of Eq. (3) to make $\rho(\mathbf{r})$ the "independent variable."

The proof of the theorem in Eqs. (3)–(6) begins with the lemma given by one of us⁸ that features the space of N -electron antisymmetric wave functions ψ , which produce the normalized density $\rho(\mathbf{r})$. $E_v[\rho]$ is identified as

⁸Research supported, in part, by NSF Grant CHE 80-23456.

the minimum value of $\langle \psi_\rho | H | \psi_\rho \rangle / \langle \psi_\rho | \psi_\rho \rangle$ with respect to variations of ψ_ρ within this space of functions having the same ρ .⁸ The variation may be performed using the Lagrange multiplier ϵ to ensure that $\langle \psi_\rho | \psi_\rho \rangle = 1$ and the Lagrange multiplier function $\lambda(\mathbf{r})$ to make $\rho(\mathbf{r}) = \langle \psi_\rho | \hat{\rho}(\mathbf{r}) | \psi_\rho \rangle$ at each point \mathbf{r} .⁹ Thus, the variation is

$$\delta \{ \langle \psi_\rho | H | \psi_\rho \rangle - \epsilon \langle \psi_\rho | \psi_\rho \rangle - \int d\mathbf{r} \lambda(\mathbf{r}) [\rho(\mathbf{r}) - \langle \psi_\rho | \hat{\rho}(\mathbf{r}) | \psi_\rho \rangle] \} = 0. \quad (7)$$

Variation with respect to ψ_ρ^* gives

$$\left[H + \sum_{i=1}^N \lambda_i(\mathbf{r}_i) \right] \psi_\rho = \epsilon \psi_\rho, \quad (8)$$

so that multiplication by $\int \psi_\rho^*$ yields

$$\begin{aligned} \epsilon &= \langle \psi_\rho | H + \Lambda | \psi_\rho \rangle / \langle \psi_\rho | \psi_\rho \rangle \\ &= \langle \psi_\rho | H | \psi_\rho \rangle / \langle \psi_\rho | \psi_\rho \rangle + \int d\mathbf{r} \lambda(\mathbf{r}) \rho(\mathbf{r}). \end{aligned} \quad (9)$$

For $\rho(\mathbf{r})$ v -representable the minimum value of Eq. (9) occurs for the ground state $\psi_\rho[\lambda]$ of Eqs. (3)–(5). (If not, ϵ is the lowest for some symmetry.) The universal relation between $\lambda + v$ and ρ implies that $E_v[\rho]$, the minimum value of $\langle \psi_\rho | H | \psi_\rho \rangle / \langle \psi_\rho | \psi_\rho \rangle$, is just the quantity quoted in Eqs. (3)–(5).

Equation (6) is readily verified by first using the functional Hellmann–Feynman theorem as follows: The functional derivative of Eq. (8) with respect to $\lambda(\mathbf{r})$ is [using $\sum_{i=1}^N \lambda_i(\mathbf{r}_i) = \int d\mathbf{r} \lambda(\mathbf{r}) \hat{\rho}(\mathbf{r})$]:

$$\begin{aligned} \left[H + \int d\mathbf{r}' \lambda(\mathbf{r}') \hat{\rho}(\mathbf{r}') \right] \frac{\delta \psi_\rho}{\delta \lambda(\mathbf{r})} \\ + \hat{\rho}(\mathbf{r}) \psi_\rho = \frac{\delta E_\rho[\lambda]}{\delta \lambda(\mathbf{r})} \psi_\rho + E_\rho[\lambda] \frac{\delta \psi_\rho}{\delta \lambda(\mathbf{r})}, \end{aligned} \quad (10)$$

where we have used the equality $\epsilon \equiv E_\rho[\lambda]$. Multiplication of Eq. (10) by $\int \psi_\rho^*$ and use of the Schrödinger equation (8) results in

$$\frac{\delta E_\rho[\lambda]}{\delta \lambda(\mathbf{r})} = \langle \psi_\rho | \hat{\rho}(\mathbf{r}) | \psi_\rho \rangle / \langle \psi_\rho | \psi_\rho \rangle \equiv \rho(\mathbf{r}). \quad (11)$$

The functional derivative of Eq. (5) with respect to $\rho(\mathbf{r})$ is then

$$\begin{aligned} \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} &= \int d\mathbf{r}' \frac{\delta E_\rho[\lambda]}{\delta \lambda(\mathbf{r}')} \frac{\delta \lambda(\mathbf{r}')}{\delta \rho(\mathbf{r})} \\ &\quad - \int d\mathbf{r}' \left[\delta(\mathbf{r} - \mathbf{r}') \lambda(\mathbf{r}') + \rho(\mathbf{r}') \frac{\delta \lambda(\mathbf{r}')}{\delta \rho(\mathbf{r})} \right], \end{aligned} \quad (12)$$

where the functional relation $\lambda = \lambda(\mathbf{r}'; [\rho])$ is used on the

right in Eq. (12). Substitution of Eq. (11) into Eq. (12) and performing the trivial delta function integral produces Eq. (6) as stated. Since $\lambda(\mathbf{r}'; [\rho_0])$ vanishes for ρ_0 , the exact ground state density, Eq. (6) verifies the HK variational principle

$$\left. \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho_0} \equiv 0.$$

The calculation of the exact $E_v[\rho]$ in Eqs. (3)–(5) requires the ground state energy and density for an arbitrary “total” external potential $v + \lambda$ as well as the inversion of Eq. (4) to find the particular $\lambda(\mathbf{r}; [\rho])$ which gives $\rho(\mathbf{r})$, both rather formidable tasks. Approximate functions $E_v[\rho]$ may be evaluated directly from Eqs. (3)–(5) by a variety of methods. Here we now concentrate on demonstrating how Eqs. (3)–(5) can be used to represent $E_v[\rho]$ as an explicit Taylor expansion in powers of $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0(\mathbf{r})$.

Basically, we desire $E_v[\rho]$ for ρ near the ground state value ρ_0 , where λ in Eqs. (3) and (4) is absent. (An approximate form would involve ρ near a SCF value ρ_{SCF} .) Hence, we may evaluate Eq. (3) by a perturbation expansion in the “small” λ . To lowest order in λ this yields

$$E_\rho[\lambda] = E + \langle \psi_0 | \Lambda | \psi_0 \rangle + \sum_{a \neq 0} |\langle \psi_0 | \Lambda | \psi_a \rangle|^2 (E_0 - E_a)^{-1} + O(\lambda^3), \quad (13)$$

where ψ_a are eigenfunctions of H with energy E_a . Similarly Eq. (4) is given as

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \int d\mathbf{r}' K^{-1}(\mathbf{r}, \mathbf{r}') \lambda(\mathbf{r}') + O(\lambda^2), \quad (14)$$

where K^{-1} is the density–density correlation function¹⁰ which may be evaluated by many-body methods,¹¹

$$K^{-1}(\mathbf{r}, \mathbf{r}') = 2 \text{Re} \sum_{a \neq 0} \rho_{0a}(\mathbf{r}) \rho_{a0}(\mathbf{r}') (E_0 - E_a)^{-1}, \quad (15)$$

with $\rho_{0a}(\mathbf{r}) \equiv \langle \psi_0 | \hat{\rho}(\mathbf{r}) | \psi_a \rangle$, etc. Defining the inverse,

$$\int K(\mathbf{r}, \mathbf{r}') K^{-1}(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}''), \quad (16)$$

enables Eq. (14) to be inverted to give

$$\lambda(\mathbf{r}) = \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') [\rho(\mathbf{r}') - \rho_0(\mathbf{r}')] + O[(\delta\rho)^2]. \quad (17)$$

Higher terms in the series (14) and (17) may readily be obtained. For instance, the $O(\lambda^2)$ terms in Eq. (14) can be written in the form $\int d\mathbf{r}' d\mathbf{r}'' K_3^{-1}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \lambda(\mathbf{r}') \lambda(\mathbf{r}'')$, where K_3^{-1} is found to be

$$\begin{aligned} K_3^{-1}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &= \sum_{a, b \neq 0} [\rho_{0a}(\mathbf{r}) \rho_{ab}(\mathbf{r}') \rho_{b0}(\mathbf{r}'') + \rho_{0a}(\mathbf{r}') \rho_{ab}(\mathbf{r}) \rho_{b0}(\mathbf{r}'') + \rho_{0a}(\mathbf{r}') \rho_{ab}(\mathbf{r}'') \rho_{b0}(\mathbf{r})] (E_0 - E_a)^{-1} (E_0 - E_b)^{-1} \\ &\quad - \sum_{a \neq 0} [\rho_{0a}(\mathbf{r}) \rho_{a0}(\mathbf{r}') \rho_0(\mathbf{r}'') + \rho_{0a}(\mathbf{r}') \rho_{a0}(\mathbf{r}) \rho_0(\mathbf{r}'') + \rho_{0a}(\mathbf{r}') \rho_{a0}(\mathbf{r}'') \rho_0(\mathbf{r})] (E_0 - E_a)^{-2}. \end{aligned} \quad (18)$$

Use of the $O(\lambda^2)$ term in Eq. (14) multiplication by $\int K$ and iteration with respect to λ leads to the $O[(\delta\rho)^2]$ contribution to Eq. (17) as

$$- \int d\mathbf{r} K(\mathbf{r}, \mathbf{r}_1) K_3^{-1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) K(\mathbf{r}_2, \mathbf{r}') \delta\rho(\mathbf{r}') K(\mathbf{r}_3, \mathbf{r}'') \delta\rho(\mathbf{r}'') d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}' d\mathbf{r}'' \equiv - \int d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \delta\rho(\mathbf{r}') \delta\rho(\mathbf{r}''), \quad (19)$$

etc. This approach provides, to our knowledge, the first general scheme for calculating $E_v[\rho]$ from first principles.

Explicit approximate forms for $E_v[\rho]$ can also be generated by use of the variational procedure (7)–(9), where ψ_ρ is further restricted to some class of wave functions such as those generated by single determinantal, multi-configurational, coupled cluster, etc., approximations to ψ_ρ . These approximate representations of $E_v[\rho]$ as well as those generated by many-body calculations of ρ_0 , K , K_3 , etc., appear to still require the determination of $\lambda(\mathbf{r}; [\rho])$ by an analog of the above perturbation expansion in λ . The derivation of a closed form for $E_v[\rho]$, not involving an expansion in powers of $\delta\rho$, requires methods to invert Eq. (4) by alternative nonperturbative means.

The exact $\delta\rho$ expansion form for $E_v[\rho]$ can be obtained by substituting Eq. (17) into Eq. (13) or more directly by integrating Eq. (6) with (17) to give¹²

$$E_v[\rho] = E_v[\rho_0] - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \\ - \frac{1}{3} \iiint d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \delta\rho(\mathbf{r}) \\ \times \delta\rho(\mathbf{r}') \delta\rho(\mathbf{r}'') + O[(\delta\rho)^4]. \quad (20)$$

As with most perturbation based quantities, Eq. (20) is probably only asymptotic, being valid for "small" $\delta\rho$. The general theory, however, of Eqs. (3)–(6) is exact and may permit the derivation of a more desirable closed form for $E_v[\rho]$.

The kernel K^{-1} in Eq. (15) is nonpositive since for any function $\phi(\mathbf{r})$ we have

$$\int d\mathbf{r} d\mathbf{r}' \phi^*(\mathbf{r}) K^{-1}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') \\ = 2 \sum_{\alpha \neq 0} \left| \int d\mathbf{r} \phi^*(\mathbf{r}) \rho_{0\alpha}(\mathbf{r}) \right|^2 (E_0 - E_\alpha)^{-1}, \quad (21)$$

which is nonpositive. By expressing $K^{-1}(\mathbf{r}, \mathbf{r}')$ in an eigenfunction expansion $K^{-1}\chi_j = k_j \chi_j$, Eq. (21) implies $k_j < 0$. Then the inversion (16) may be performed to obtain an eigenfunction expansion of K . This result can

be used to demonstrate that for arbitrary $\delta\rho$, for which the integrals are well defined, the quadratic term in Eq. (20)

$$- \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \geq 0, \quad (22)$$

so indeed $E_v[\rho_0]$ is a true minimum as required by the HK theorem.

It should come as no surprise that the *exact* calculation of $E_v[\rho]$ in Eqs. (20) or (5) is equivalent to the *exact* solution of the full many-electron Schrödinger equation. The HK theorem only provides knowledge of the existence of $E_v[\rho]$, while the present theory produces an explicit representation of $E_v[\rho]$ that may be used in the theoretical analyses and is amenable to direct approximate numerical calculations.

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