

Ab initio methods in solid state physics

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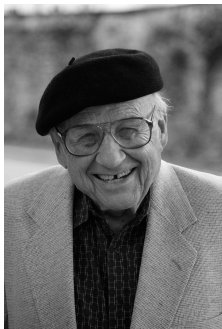
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March 4, 2021

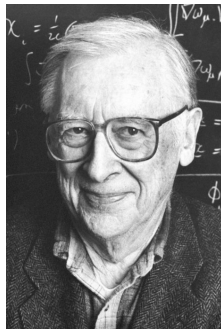
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The Nobel Prize in Chemistry 1998



Walter Kohn (1923-2016)



John A. Pople (1925-2004)

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

Inhomogeneous Electron Gas*

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Hohenberg-Kohn theorems

We consider the general Hamiltonian of the N -electron system

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{\text{ext}}(\mathbf{r}), \quad (1)$$

which gives the total energy in the normalized ground state $|\Psi\rangle$

$$E = \langle \Psi | H | \Psi \rangle = \langle T \rangle + \langle U \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}). \quad (2)$$

Theorem 1. The external potential $V_{\text{ext}}(\mathbf{r})$, and hence the total energy, is determined uniquely by the ground state electron density $n_0(\mathbf{r})$.

The proof proceeds by *reductio ad absurdum*. Let there be two different external potentials, V_{ext}^1 and V_{ext}^2 , that give rise to the same density $n_0(\mathbf{r})$. The associated Hamiltonians, H_1 and H_2 , will therefore have different ground state wavefunctions, Ψ_1 and Ψ_2 , that each yield the same density $n_0(\mathbf{r})$.

Hohenberg-Kohn theorems

$$E_1 = \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle = \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | (H_1 - H_2) | \Psi_2 \rangle, \quad (3)$$

$$E_1 < E_2 + \int d\mathbf{r} [V_{\text{ext}}^1(\mathbf{r}) - V_{\text{ext}}^2(\mathbf{r})] n_0(\mathbf{r}). \quad (4)$$

By interchanging the indices $1 \leftrightarrow 2$ we get

$$E_2 < E_1 + \int d\mathbf{r} [V_{\text{ext}}^2(\mathbf{r}) - V_{\text{ext}}^1(\mathbf{r})] n_0(\mathbf{r}). \quad (5)$$

If we add together (4) and (5) we arrive at the contradictory inequality

$$E_1 + E_2 < E_1 + E_2. \quad (6)$$

The ground state density uniquely determines the external potential V_{ext} (to within an additive constant). The electrons determine the positions of the nuclei in a system, and also all ground state electronic properties, because V_{ext} completely defines the hamiltonian H and the ground state $|\Psi\rangle$.

Hohenberg-Kohn theorems

Theorem 2. For any particular external potential $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of the energy functional $E[n]$, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$

$$E[n] = F[n] + E_{\text{ext}}[n] = F[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) = \min, \quad (7)$$

where $F[n] = \langle T \rangle + \langle U \rangle$ is a universal functional of density $n(\mathbf{r})$ – functional means "function of a function", which maps functions into real numbers.

To prove it we consider a different density $n'(\mathbf{r})$, which corresponds to a different wavefunction Ψ' , and we obtain

$$E[n] = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = F[n'] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n'(\mathbf{r}) = E[n']. \quad (8)$$

The energy given by (7) evaluated for the correct ground state density $n_0(\mathbf{r})$ is lower than the value of energy for any other density.

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

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(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Kohn-Sham energy functional

The exact ground state density can be represented by the ground state density of the auxiliary system of non-interacting electrons. The total energy is the functional of electron density $n(\mathbf{r})$, which can be written in the form

$$E[n] = T[n] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n], \quad (9)$$

where $T[n]$ is the kinetic energy

$$T[n] = -\frac{\hbar^2}{2m} \sum_{i,\sigma} \int d\mathbf{r} \psi_i^{\sigma*}(\mathbf{r}) \nabla^2 \psi_i^{\sigma}(\mathbf{r}), \quad (10)$$

$E_{\text{H}}[n]$ is the Hartree energy

$$E_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (11)$$

and $E_{\text{xc}}[n]$ is the exchange-correlation energy, which includes all other interactions between electrons besides the Hartree interaction.

Kohn-Sham equation

Using the variational principle

$$\frac{\delta}{\delta \psi_i^{\sigma*}} (E[n] - \sum_{i,\sigma} \varepsilon_{i\sigma} \int d\mathbf{r} |\psi_i^\sigma(\mathbf{r})|^2) = 0, \quad (12)$$

and applying $n(\mathbf{r}) = \sum_{i\sigma} |\psi_i^\sigma(\mathbf{r})|^2$ and $\frac{\delta}{\delta \psi_i^{\sigma*}} = \frac{\delta}{\delta n} \frac{\delta n}{\delta \psi_i^{\sigma*}}$, we obtain

$$\frac{\delta T[n]}{\delta \psi_i^{\sigma*}} + \frac{\delta}{\delta n} \left(\int d\mathbf{r} V_{\text{ext}} n(\mathbf{r}) + E_{\text{H}}[n] + E_{\text{xc}}[n] \right) \frac{\delta n}{\delta \psi_i^{\sigma*}} - \varepsilon_{i\sigma} \frac{\delta}{\delta \psi_i^{\sigma*}} \sum_{j,\sigma'} \int d\mathbf{r} |\psi_j^{\sigma'}(\mathbf{r})|^2 = 0, \quad (13)$$

which gives the Kohn-Sham (KS) equation

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{KS}}(\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) = \varepsilon_{i\sigma} \psi_i^\sigma(\mathbf{r}), \quad (14)$$

with the effective potential

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[n]}{\delta n}. \quad (15)$$

Knowing the KS eigenenergies $\varepsilon_{i\sigma}$ and density $n(\mathbf{r})$, the total energy is given by

$$E = \sum_{i\sigma} f_{i\sigma} \varepsilon_{i\sigma} - \int d\mathbf{r} n(\mathbf{r}) V_{KS}(\mathbf{r}) + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n], \quad (16)$$

where $f_{i\sigma}$ are the occupations of the KS states. One-electron KS energies do not have unambiguous physical meaning. However, we can relate them with a change of total energy due to a change of electron occupation

$$\varepsilon_{i\sigma} = \frac{\partial E}{\partial f_{i\sigma}} = \left(\frac{\partial E}{\partial f_{i\sigma}} \right)_n + \int d\mathbf{r} \frac{\delta E}{\delta n} \frac{\partial n}{\partial f_{i\sigma}} = \left(\frac{\partial E}{\partial f_{i\sigma}} \right)_n, \quad (17)$$

which is true for the ground state ($\delta E / \delta n = 0$). This is the Janak theorem:
J. F. Janak, Phys. Rev. B **18**, 7165 (1977).

By applying this formula to the highest occupied state, we can obtain the ionization energy – the energy required for removing one electron from the system.

Local density approximation (LDA)

In LDA, the exchange-correlation energy at a point \mathbf{r} is equal to the exchange-correlation of the homogeneous electron gas of the same density n as the density at this point $n(\mathbf{r})$. The exchange-correlation functional is written

$$E_{\text{xc}}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n) = \int d\mathbf{r} n(\mathbf{r}) (\varepsilon_{\text{x}}(n) + \varepsilon_{\text{c}}(n)), \quad (18)$$

where $\varepsilon_{\text{xc}}(n)$ is the exchange-correlation energy per one electron in the homogeneous gas with the density n . It can be generalized to systems with the spin polarization with spin-up n_{\uparrow} and spin-down n_{\downarrow} densities (local spin density approximation)

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n_{\uparrow}, n_{\downarrow}), \quad (19)$$

where $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$. The exchange-correlation potential depends on spin

$$V_{\text{xc}}^{\sigma} = \frac{\delta E_{\text{xc}}}{\delta n_{\sigma}} = \varepsilon_{\text{xc}} + n_{\sigma} \frac{\partial \varepsilon_{\text{xc}}}{\partial n_{\sigma}}. \quad (20)$$

Local density approximation (LDA)

LDA is accurate in the limit of slowly varying density, which corresponds to the condition

$$\frac{q}{k_F} \ll 1, \quad (21)$$

where q is a measure of inhomogeneity in the system

$$q = \frac{|\nabla k_F|}{2k_F}, \quad (22)$$

and the Fermi wave vector k_F at each point \mathbf{r} is related to the local electron density by the formula

$$k_F = [3\pi^2 n(\mathbf{r})]^{1/3}. \quad (23)$$

Local density approximation (LDA)

The exchange energy per one electron was derived for the electron gas

$$\varepsilon_x(n_\sigma) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n_\sigma^{\frac{1}{3}}, \quad (24)$$

which gives the exchange potential

$$V_x^\sigma = \varepsilon_x + n_\sigma \frac{\partial \varepsilon_x}{\partial n_\sigma} = -\left(\frac{3}{\pi} \right)^{\frac{1}{3}} n_\sigma^{\frac{1}{3}}. \quad (25)$$

The correlation energy was accurately obtained numerically by the Quantum Monte Carlo method, and fitted by the analytical formula, e.g. Perdew-Zunger parametrization: J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981),

$$\varepsilon_c(r_s) = \begin{cases} -0.048 + 0.031 \ln(r_s) - 0.0116r_s + 0.002r_s \ln(r_s), & r_s < 1 \\ -0.1423/(1 + 1.0529\sqrt{r_s} + 0.3334r_s), & r_s > 1. \end{cases} \quad (26)$$

Generalized gradient approximation (GGA)

In GGA, the exchange-correlation energy is a functional of electronic density and its gradients

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}). \quad (27)$$

The exchange part for the non-spin-polarized system can be written in the form

$$E_{\text{x}}[n] = \int d\mathbf{r} n \varepsilon_{\text{x}}(n) F_{\text{x}}(s), \quad (28)$$

where

$$s = \frac{|\nabla n|}{2k_{\text{F}} n} \quad (29)$$

is the scaled dimensionless gradient of electronic density. It can be extended to spin-polarized systems using the following dependence

$$E_{\text{x}}[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2}(E_{\text{x}}[2n_{\uparrow}] + E_{\text{x}}[2n_{\downarrow}]). \quad (30)$$

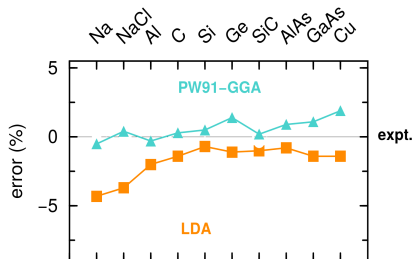
Generalized gradient approximation (GGA)

J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992) (PW91).

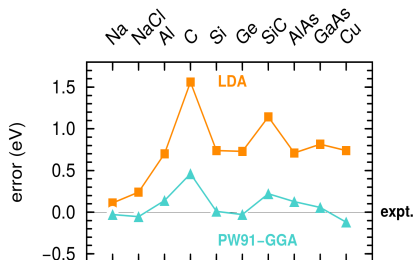
J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996) (PBE).

Lattice constant



Cohesion energy



Self-interaction problem

One electron system – hydrogen atom ($E = T + E_{\text{ext}}$)

E_{H} – exact

$E_{\text{x}}, E_{\text{c}}$ – approximate

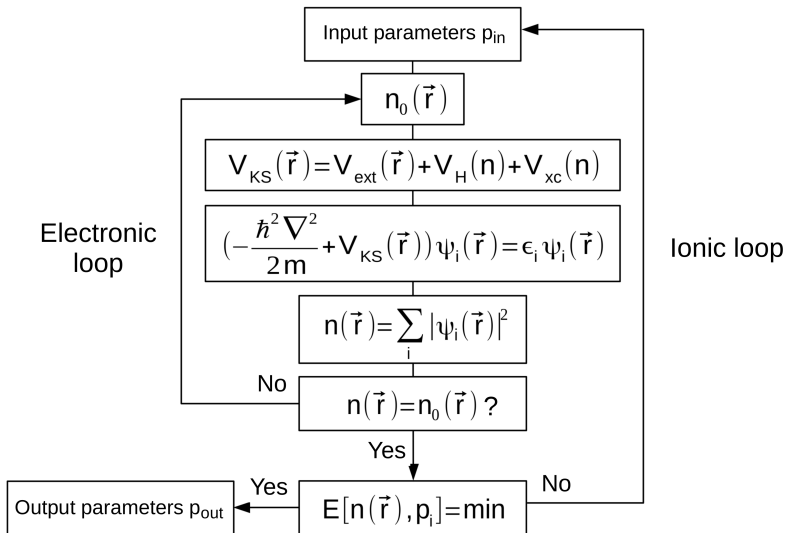
$E_{\text{H}} \neq -(E_{\text{x}} + E_{\text{c}}) \rightarrow E_{\text{H}} + E_{\text{x}} + E_{\text{c}} \neq 0$ (self-interaction)

Table : Comparison of the exchange and correlation energies (in eV) for selected atoms with the exact values.

	LDA		GGA (PBE)		Exact	
Atom	E_{x}	E_{c}	E_{x}	E_{c}	E_{x}	E_{c}
H	-0.2680	-0.0222	-0.3059	-0.0060	-0.3125	0.0000
He	-0.8840	-0.1125	-1.0136	-0.0420	-1.0258	-0.0420
Be	-2.3124	-0.2240	-2.6358	-0.0856	-2.6658	-0.0950
N	-5.9080	-0.4268	-6.5521	-0.1799	-6.6044	-0.1858
Ne	-11.0335	-0.7428	-12.0667	-0.3513	-12.1050	-0.3939

In the Hartree-Fock approximation, the exchange self-interaction cancels perfectly with the Hartree self-interaction ($E_{\text{x}} = -E_{\text{H}}$), so the net self-interaction is zero.

Self-consistent iterative scheme



Numerical mixing scheme

Minimization procedure can be accelerated by mixing electronic density obtained in the subsequent steps. In the simplest approach, the input density n_{i+1}^{in} in step $i + 1$ can be calculated as the linear modification of density in step i

$$n_{i+1}^{\text{in}} = n_i^{\text{in}} + \alpha(n_i^{\text{out}} - n_i^{\text{in}}), \quad (31)$$

where α is a linear coefficient, n_i^{in} and n_i^{out} are the input and output densities in step i . The constant value of α does not provide the optimal speed of convergence. In the most popular Broyden method, the linear coefficient is obtained from the Jacobian $\alpha = -J_i^{-1}$, which is optimized at each step of the iteration procedure ($x_{i+1} - x_i = -J_i^{-1}R_i$).

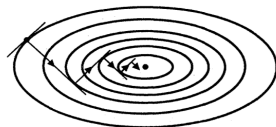
Minimization procedure – conjugate-gradients technique

The conjugate-gradients technique provides a simple and effective procedure for implementation of the minimization procedure ($F(x) = \min$). The initial direction is taken to be the negative of the gradient at the starting point. A subsequent conjugate direction is then constructed from a linear combination of the new gradient and the previous direction that minimized $F(x)$.

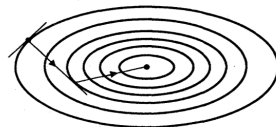
Schematic illustration of two methods of convergence to the center of an anisotropic harmonic potential. Top: steepest-descent method requires many steps to converge. Bottom: Conjugate-gradients method allows convergence in two steps.

M. C. Payne, *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

STEEPEST DESCENTS



CONJUGATE GRADIENT



Hellmann-Feynman theorem

H. Hellmann, *Einführung in die Quantenchemie*, Leipzig, Franz Deuticke, 1937.
R. Feynman, Phys. Rev. **56**, 340 (1939).

The force acting on a nucleus at position \mathbf{R}_i is equal

$$\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i}, \quad (32)$$

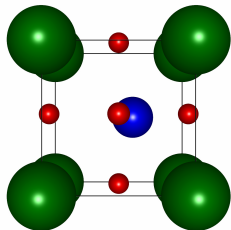
where $E = \langle \Psi | H | \Psi \rangle$ is the total energy of the system. Using the first-order perturbation theory, we get

$$\mathbf{F}_i = -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_i} | \Psi \rangle - \langle \frac{\partial \Psi}{\partial \mathbf{R}_i} | H | \Psi \rangle - \langle \Psi | H | \frac{\partial \Psi}{\partial \mathbf{R}_i} \rangle. \quad (33)$$

For the ground state $|\Psi\rangle$, the second and third terms are equal to zero, and we obtain

$$\boxed{\mathbf{F}_i = -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_i} | \Psi \rangle = -\int d\mathbf{r} n(\mathbf{r}) \frac{\partial V_{\text{ext}}}{\partial \mathbf{R}_i}.} \quad (34)$$

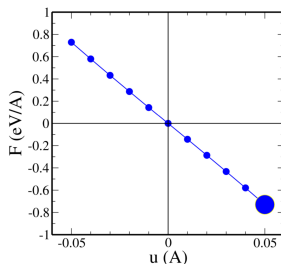
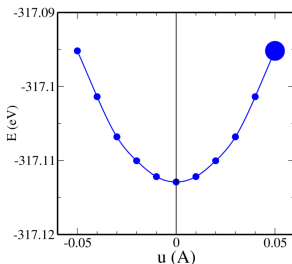
Hellmann-Feynman theorem – example: BaTiO₃



In the harmonic approximation, the total energy E is a quadratic function of atomic displacement u

$$E(u) = E_0 + \frac{1}{2}ku^2, \quad (35)$$

$$F(u) = -\frac{\partial E}{\partial u} = -ku. \quad (36)$$



Conditions of equilibrium states

- 1 In the equilibrium state ($E = \min$), forces acting on all atoms at positions \mathbf{R}_i should be equal zero

$$\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i} = 0. \quad (37)$$

In practice, forces should be small enough to fulfil convergence criteria.

- 2 Macroscopic stress in the system should be equal to the stress induced by a given external pressure p . For the fully relaxed structure, we assume $p = 0$. The stress tensor is determined by the derivative of total energy with respect to strain tensor

$$\sigma_{\alpha\beta} = -\frac{1}{V} \frac{\partial E}{\partial u_{\alpha\beta}}, \quad (38)$$

where V is the system volume. Strain tensor is a symmetrical tensor of derivative of displacement vectors $\mathbf{u} = \mathbf{r} - \mathbf{r}'$ with respect a position \mathbf{r} . Under hydrostatic conditions, pressure is connected with the stress tensor by the relation $p = -\frac{1}{2} \sum_{\alpha} \sigma_{\alpha\alpha}$.