



Self-consistent equations [Kohn-Sham, 1965]

$$V_{eff}(\mathbf{r}, \mathbf{R}) = V_{ext}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r}, \mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2\sum_{i} |\phi_i(\mathbf{r})|^2$$



It is as simple as a Mean-field approach but it is exact ! $E_{xc}[n]$ is not known exactly \rightarrow approximations



Kohn-Sham eigenvalues

The eigenvalues are Lagrange multipliers of the *auxiliary* unphysical system. No formal justification to give them a physical meaning.

<u>Except for the highest occupied molecular orbital (HOMO)</u> <u>in a finite system for which</u>

 $-\varepsilon_{HOMO} = IP$

exactly for the exact functional !

The proof relies on the way the charge density decays as one moves away from a finite system.







 $EA_i = E(N, 0) - E(N + 1, i) = h\nu - Ekin$



Janak's theorem

The theory can be extended to *partial occupations*

$$n(\mathbf{r}) = \sum_{i} f_{i} |\phi_{i}(\mathbf{r})|^{2}, \quad 0 \leq f_{i} \leq 1, \quad \sum_{i} f_{i} = N$$
$$T_{s} = \sum_{i} f_{i} \langle \phi_{i} | -\frac{\hbar^{2}}{2m} \nabla^{2} |\phi_{i} \rangle$$
$$E(N) = \min_{n \to N} \left\{ T_{s}[n] + E_{H}[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\}$$

It can be shown that

$$\frac{\partial E}{\partial f_i} = \varepsilon_i$$

 $f_i = 1 \text{ if } \varepsilon_i < \mu, \quad 0 \le f_i \le 1 \text{ if } \varepsilon_i = \mu, \quad f_i = 0 \text{ if } \varepsilon_i > \mu$

PHYSICAL REVIEW

1 MARCH 1965

Thermal Properties of the Inhomogeneous Electron Gas*

N. DAVID MERMIN[†]

Department of Physics, University of California, San Diego, La Jolla, California (Received 8 October 1964)

A variational property of the ground-state energy of an electron gas in an external potential $v(\mathbf{r})$, derived by Hohenberg and Kohn, is extended to nonzero temperatures. It is first shown that in the grand canonical ensemble at a given temperature and chemical potential, no two $v(\mathbf{r})$ lead to the same equilibrium density. This fact enables one to define a functional of the density $F[n(\mathbf{r})]$ independent of $v(\mathbf{r})$, such that the quantity $\Omega = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ is at a minimum and equal to the grand potential when $n(\mathbf{r})$ is the equilibrium density in the grand ensemble in the presence of $v(\mathbf{r})$.

$$\begin{split} F[n(\mathbf{r})] &= \inf_{\rho \to n(\mathbf{r})} \operatorname{Tr} \left[\rho \left(T + W_{ee} \right) + \frac{1}{\beta} \rho \ln \rho \right] \\ T_s[n(\mathbf{r})] &= \inf_{\rho \to n(\mathbf{r})} \operatorname{Tr} \left[\rho \left(T + \frac{1}{\beta} \rho \ln \rho \right) \right] \end{split}$$



Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy

John P. Perdew

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

and

Robert G. Parr

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

and

Mel Levy

Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

and

Jose L. Balduz, Jr.

Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 16 August 1982)

The Hohenberg-Kohn theorem is extended to fractional electron number N, for an isolated open system described by a statistical mixture. The curve of lowest average energy E_N versus N is found to be a series of straight line segments with slope discontinuities at integral N. As N increases through an integer M, the chemical potential and the highest occupied Kohn-Sham orbital energy both jump from $E_M - E_{M-1}$ to $E_{M+1} - E_M$. The exchange-correlation potential $\delta E_{\rm xc}/\delta n(\vec{r})$ jumps by the same constant, and $\lim_{r \to \infty} \delta E_{\rm xc}/\delta n(\vec{r}) \ge 0$.



Derivative Discontinuity of the Energy Functional JP Perdew, RG Parr, M Levy, JL Balduz, PRL **49**,1691 (1982)

The theory can be extended to systems with a fractional number of electrons in contact with a reservoir.

The energy as a function of the number of electrons in a finite system is piece-wise linear .

The corresponding slope equals the IP or the EA depending on whether $~\omega<0$ or $~\omega>0~$ with $~N_{el}=N+\omega$

As the number of electrons in the system crosses an integer value the (xc) potential experiences a jump.



Kohn-Sham gap problem ?

The eigenvalues are Lagrange multipliers of the *auxiliary* unphysical system.

No formal justification to give them a physical meaning.

Still it's common practice to analyze the band structure of a system and compare it with the experimental results obtained from photoemission and inverse photoemission experiments... with generally favorable agreement but a systematic underestimation of the fundamental energy gap.

Is this an LDA problem ... or a DFT feature ?





Kohn-Sham gap problem ?



Kohn-Sham gap problem ? ... and/or HF gap problem ?



Physical Content of the Exact Kohn-Sham Orbital Energies: Band Gaps and Derivative Discontinuities

John P. Perdew

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106, and Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

and

Mel Levy

Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118 (Received 17 June 1983)

The local-density approximation for the exchange-correlation potential underestimates the fundamental band gaps of semiconductors and insulators by about 40%. It is argued here that underestimation of the gap width is also to be expected from the unknown *exact* potential of Kohn-Sham density-functional theory, because of derivative discontinuities of the exchange-correlation energy. The need for an energy-dependent potential in band theory is emphasized. The center of the gap, however, is predicted exactly by the Kohn-Sham band structure.





Figure 4. Spin-up exchange potentials, V_{xt} , for Na⁺ in exchange-only approximation for filled 2p subshells and empty 3s subshells (lower curve) and for partially filled 3st state with $f_{3st} = 10^{-2}$. Also $V_{xt}(f_{3st} = 10^{-2}) - V_{xt}(f_{3st} = 0)$ (right ordinate axis).

JB Krieger, Y Li & GJ Iafrate, in *Density Functional Theory*, Plenum press, 1995 EKU Gross and RM Drezler Eds





JP Perdew

"What do the Kohn-Sham orbital energies mean ? How do atoms Dissociate ?" p. 265 in Density Functional Methods in Physics, NATO ASI series 123 (1983) RM Dreizler & J da Providenza Eds. Adiabatic approximation

Independent electrons in an effective potential

Hartree-Fock

Density Functional Theory

MBPT - GW





MBPT

GW approximation

PHYSICAL REVIEW

VOLUME 139, NUMBER 3A p. 796 2 AUGUST 1965

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN[†]

Argonne National Laboratory, Argonne, Illinois (Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in





L. Hedin, S. Lundqvist, Solid State Phys. 23 (1969) 1.

The Green's Function

The Green's function is the propagation amplitude for an added electron or an added hole

$$iG(rt, r't') = \begin{cases} \langle N, 0 | \Psi(r, t) \Psi^{\dagger}(r', t') | N, 0 \rangle, & t > t' \\ -\langle N, 0 | \Psi^{\dagger}(r', t') \Psi(r, t) | N, 0 \rangle, & t' > t \end{cases}$$

 $iG(r,r',t-t') = \langle N,0|T[\Psi(r,t),\Psi^{\dagger}(r',t')]|N,0\rangle$

$$\rho(r,t) = \langle N, 0 | \Psi^+(r,t) \Psi(r,t) | N, 0 \rangle = -iG(rt,rt^+)$$

$$\gamma(r,r',t) = \langle N, 0 | \Psi^+(r,t) \Psi(r',t) | N, 0 \rangle = -iG(r't,rt^+)$$



$$\begin{split} \text{The Green's Function} \\ iG(r,r',t-t') &= \langle N, 0 | T[\Psi(r,t), \Psi^{\dagger}(r',t')] | N, 0 \rangle \\ \hline t > t' \\ iG(r,r',t-t') &= \sum_{s} \langle N, 0 | \Psi(r,t) | N+1, s \rangle \langle N+1, s | \Psi^{\dagger}(r',t') | N, 0 \rangle \\ &= \sum_{s} e^{-i(E(N+1,s)-E(N,0))(t-t')} \langle N, 0 | \Psi(r) | N+1, s \rangle \langle N+1, s | \Psi^{\dagger}(r') | N, 0 \rangle \\ \hline t' > t \\ iG(r,r',t-t') &= -\sum_{s} \langle N, 0 | \Psi^{\dagger}(r',t') | N-1, s \rangle \langle N-1, s | \Psi(r,t) | N, 0 \rangle \\ &= -\sum_{s} e^{-i(E(N,0)-E(N-1,s))(t-t')} \langle N, 0 | \Psi^{\dagger}(r') | N-1, s \rangle \langle N-1, s | \Psi(r,t) | N, 0 \rangle \\ \hline \end{split}$$

The Green's Function

$$G(r, r', \omega) = \sum_{s} \frac{J_s(r)J_s(r)}{\omega - \varepsilon_s + i\eta\operatorname{sign}(\varepsilon_s - \mu)}$$

$$\varepsilon_s = \begin{cases} E(N+1,s) - E(N,0) & -\operatorname{EAs} \\ E(N,0) - E(N-1,s) & -\operatorname{IPs} \end{cases}$$

$$f_s(r) = \langle N, 0 | \Psi(r) | N + 1, s \rangle$$
 if $\varepsilon_s > \mu$

$$f_s(r) = \langle N-1, s | \Psi(r) | N, 0 \rangle$$
 if $\varepsilon_s < \mu$

 $\mu = E(N + 1, 0) - E(N, 0)$

8

μ

......



What is W?

Interaction between electrons in vacuum:

$$v(\mathbf{r},\mathbf{r'}) = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\mathbf{r}-\mathbf{r'}|}$$



Interaction between electrons in a homogeneous polarizable medium:





Dynamically screened interaction between electrons in a general medium:

$$W(\mathbf{r},\mathbf{r}',\omega) = \frac{e^2}{4\pi\varepsilon_0} \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',\omega)}{|\mathbf{r}''-\mathbf{r}'|}$$





Hedin's coupled equations

In the Hartree-Fock approximation we have

$$H^{HF} = H_0 + V_x$$

Where *Ho* is the hamiltonian including Hartree pot. and $V_x(\mathbf{r}, \mathbf{r}') = -\sum_{i}^{occ} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') \frac{e^2}{|\mathbf{r}, \mathbf{r}'|} = iG^{HF}(\mathbf{r}, t; \mathbf{r}', t^+) \frac{e^2}{|\mathbf{r}, \mathbf{r}'|}$

from

$$(\varepsilon - H^{HF})G^{HF} = I, \qquad (\varepsilon - H_0)G_0 = I$$

we get

$$G^{HF} = G_0 + G_0 V_x G^{HF}$$

More in general we can write

$$G(12) = G_0(12) + \int d34G_0(13)\Sigma(34)G(42)$$



Hedin's coupled equations

$$\Sigma(12) = i \int d34 G(13) W(14) \Gamma(423)$$

$$G(12) = G_0(12) + \int d34 G_0(13) \Sigma(34) G(42)$$

$$\Gamma(123) = \delta(12) \delta(13) + \int d4567 \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(57) \Gamma(673)$$

$$\tilde{\chi}(12) = -i \int d34 G(13) G(41) \Gamma(342)$$

$$W(12) = v(12) + \int d34 v(13) \tilde{\chi}(34) W(42)$$



Hedin's coupled equations

$$\Sigma(12) = i \int d34 G(13) W(14) \Gamma(423)$$
self-energy

$$G(12) = G_0(12) + \int d34 G_0(13) \Sigma(34) G(42)$$
Dyson equation

$$\Gamma(123) = \delta(12) \delta(13) + \int d4567 \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(57) \Gamma(673)$$
vertex correction

$$\tilde{\chi}(12) = -i \int d34 G(13) G(41) \Gamma(342)$$
polarizability

$$W(12) = v(12) + \int d34 v(13) \tilde{\chi}(34) W(42)$$

screened Coulomb interaction



Hedin's coupled equations

$$\Sigma(12) = i \int d34 G(13) W(14) \Gamma(423)$$
self-energy

$$G(12) = G_0(12) + \int d34 G_0(13) \Sigma(34) G(42)$$
Dyson equation

$$\Gamma(123) = \delta(12) \delta(13) + \int d4567 \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(57) \Gamma(673)$$
vertex correction

$$\tilde{\chi}(12) = -i \int d34 G(13) G(41) \Gamma(342)$$
polarizability

$$W(12) = v(12) + \int d34 v(13) \tilde{\chi}(34) W(42)$$
screened Coulomb interaction

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Hedin's coupled equations

$$\Sigma(12) = iG(12)W(12)$$
self-energy

$$G(12) = G_0(12) + \int d34 G_0(13)\Sigma(34)G(42)$$
Dyson equation

$$\Gamma(123) = \delta(12)\delta(13)$$
vertex correction
 $\tilde{\chi}(12) = -iG(12)G(21)$
polarizability

$$W(12) = v(12) + \int d34 \, v(13) \tilde{\chi}(34) W(42)$$

screened Coulomb interaction

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Hedin's coupled equations

$$\Sigma(12) = iG(12)W(12)$$
self-energy

$$G(12) = G_0(12) + \int d34 G_0(13)\Sigma(34)G(42)$$
Dyson equation

$$\Gamma(123) = \delta(12)\delta(13) -$$
vertex correction

$$\tilde{\chi}(12) = -iG(12)G(21)$$
polarizability

$$W(12) = v(12) + \int d34 v(13)\tilde{\chi}(34)W(42)$$
screened Coulomb interaction

PHYSICAL REVIEW B

VOLUME 32, NUMBER 6

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15 SEPTEMBER 198

Exchange and correlation in density-functional theory

L. J. Sham

Department of Physics, University of California-San Diego, La Jolla, California 92093 (Received 15 April 1985)

Expressions for the exchange-correlation energy and potential are given in terms of the perturbation series of the Coulomb interaction. The asymptotic behavior of the exchange-correlation potential for a confined system is derived. Improvement over the local-density approximation is explored.

VOLUME 56, NUMBER 22

PHYSICAL REVIEW LETTERS

p.2415 2 Ju

2 JUNE 1986

Accurate Exchange-Correlation Potential for Silicon and Its Discontinuity on Addition of an Electron

R. W. Godby and M. Schlüter AT&T Bell Laboratories, Murray Hill, New Jersey 07974

and

L. J. Sham

Department of Physics, University of California at San Diego, La Jolla, California 92093 (Received 10 February 1986)

We obtain an accurate density-functional exchange-correlation potential, $V_{xc}(\mathbf{r})$, for silicon, from calculations of the self-energy $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$. No local-density approximation (LDA) is used for V_{xc} . The band structure with this V_{xc} is in remarkably close agreement with that obtained with the LDA, while both differ significantly from the quasiparticle spectrum of Σ . The 50% band-gap error found in LDA calculations is therefore not caused by the LDA but by the discontinuity, Δ , in the exact V_{xc} on addition of an electron.



The exact Vxc is very similar to LDA Vxc.

RW Godby, M Schlueter, and LJ Sham PRL 56, 2415 (1986)

$$\operatorname{Im} \int_{-\infty}^{\varepsilon_F} \left[G_{DFT} \left(\Sigma - V_{xc} \right) G \right]_{\mathbf{r},\mathbf{r}} d\omega = 0$$



FIG. 1. Contour plots in the (110) plane containing the zigzag bond chain of (a) the true DFT exhange-correlation potential $V_{\rm xc}$ and (b) the RPA LDA potential (Ref. 14) $V_{\rm xc}^{\rm LDA}$, in electronvolts. The close similarity illustrates the high quality of the LDA for the creation of the ground-state electron density $n(\mathbf{r})$. In each case 169 plane waves were included in the summation.



PHYSICAL REVIEW B

p.5390 VOLUME 34, NUMBER 8

Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies

Mark S. Hybertsen and Steven G. Louie Department of Physics, University of California, Berkeley, California 94720 (Received 31 March 1986)

PHYSICAL REVIEW B

VOLUME 37, NUMBER 17

p.10159

15 JUNE 1988 I

15 OCTOBER 1986

Self-energy operators and exchange-correlation potentials in semiconductors

R. W. Godby

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974 and Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

M. Schlüter AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

L. J. Sham Department of Physics, University of California at San Diego, La Jolla, California 92093 (Received 12 November 1987)



GW improves the description of energy gaps

 RW Godby, M Schlueter, & LJ Sham
 PRL 56, 2415 (1986)

 MS Hybertsen & SG Louie
 PRB 34, 5390 (1986)



<u>GW recap</u>

- The GW approximation solves the band gap problem!
- The calculations are extremely heavy, so that we resort to many additional technical approximations: method named G₀W₀
- The complexity comes from
 - Dependance upon empty states
 - Non-local operators
 - Dynamic operators that requires freq. convolutions
- There are still some other approximations like the Plasmon-Pole model...



<u>Beyond single particle excitation</u> **Bethe – Salpeter Equation**





The equation was actually first published in 1951.

Hans Bethe Edwin Ernest Salpeter 1906 - 2005 1924 - 2008 Nobel Prize for Physics (1967)

describes the bound states of a two-body

(particles) system in a formalism.

Original article : A Relativistic Equation for Bound-State Problems E.E.Salpeter and H.Bethe , Phys.Rev. 84 , 1232-1242 (1951)

$$[E_{ck} - E_{vk}]A_{vck}^{n} + \sum_{v'c'k'} \langle vck | K^{eh} | v'c'k' \rangle A_{v'c'k'}^{n} = \Omega^{n}A_{vck}^{n}$$

C.Spataru, S.Ismail Beigi "Excitonic Effects of SWNT", Phys.Rev.Lett.92 , (2004)



Beyond single particle excitation

The Bethe-Salpeter Equation

effective Schrödinger equation for the electron-hole pair

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E_{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

$$H^{e-h} = H^{diag} + H^{dir} + H^x$$

$$H_{vc\mathbf{k},v'c'\mathbf{k}'}^{diag} = \left(\varepsilon_{c_{\mathbf{k}}} - \varepsilon_{v_{\mathbf{k}}}\right)\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

$$H_{vc\mathbf{k},v'c'\mathbf{k}'}^{dir} = \int \psi_{v\mathbf{k}}(\mathbf{r})\psi_{c\mathbf{k}}^{*}(\mathbf{r}')\frac{\epsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_{v'\mathbf{k}'}^{*}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')d\mathbf{r} d\mathbf{r}'$$

$$H_{vc\mathbf{k},v'c'\mathbf{k}'}^x = \int \frac{\psi_{v'\mathbf{k}'}^*(\mathbf{r}')\psi_{c\mathbf{k}}^*(\mathbf{r})\psi_{v\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$



Beyond single particle excitation







THE END

