# Advanced DFT

Scuola Internazionale Superiore di Studi Avanzati

ma per seguir virtute e conoscenza

- General Variational Formulation
- Adiabatic Connection Formalism
- Exact Exchange
  - *Sharp-Horton, Talman-Shadwick,Sham-Shlueter, KLI*
- Fluctuation-Dissipation for Correlation (vdW aware)
  - *RPA, RPAx, ...*
- ISI Interaction Strength Interpolation
- SCE Strictly Correlated Electrons
  - *Kolmogorov optimal transport dual formulation*
- LIISA Locally Interpolated Interaction Strength Approx
- Homogeneous Electron Gas: HF, RPA, Wigner Crystal
- Lieb-Oxford Bound
- Virial Theorem and Scaling Relations
- Unambiguous Energy Densities

# Optimized Effective Potential

a.k.a.

# Exact Exchange in DFT

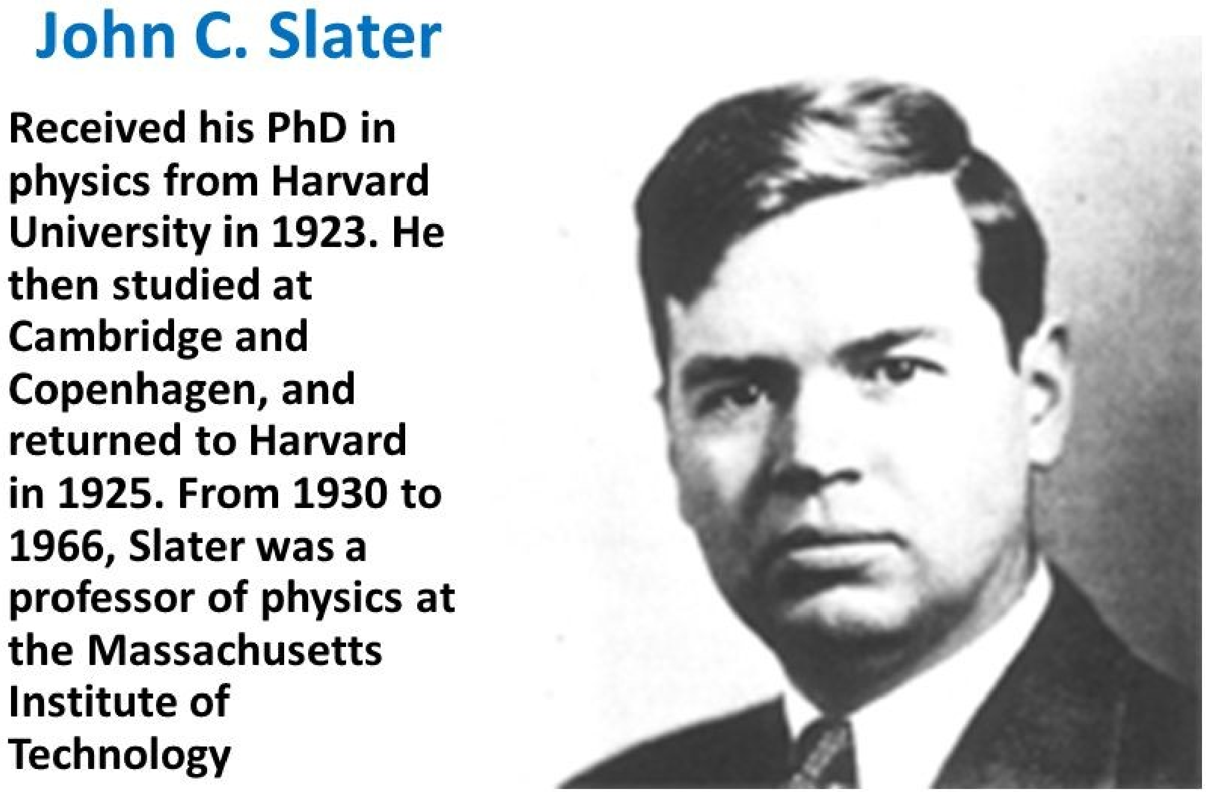
# Stater determinants

N-particle product wavefunctions (Hartree products)

$$\Phi^{\{H\}}(\mathbf{r}) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

do not belong to the Fermionic subspace;

enters



**John C. Slater**

**Received his PhD in physics from Harvard University in 1923. He then studied at Cambridge and Copenhagen, and returned to Harvard in 1925. From 1930 to 1966, Slater was a professor of physics at the Massachusetts Institute of Technology**

# Stater determinants

N-particle product wavefunctions (Hartree products)

$$\Phi^{\{H\}}(\mathbf{r}) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

do not belong to the Fermionic subspace; **are not acceptable**

$$\Phi^{\{S\}}(\mathbf{r}) = \mathcal{A}\Phi^{\{H\}}(\mathbf{r}) = \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\phi_1(r_{p_1})\phi_2(r_{p_2})...\phi_N(r_{p_N})$$

$$= \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\phi_{p_1}(r_1)\phi_{p_2}(r_2)...\phi_{p_N}(r_N)$$

**Slater determinants are acceptable Fermionic wfcs**

$$= \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \cdots & \phi_N(r_N) \end{vmatrix}$$

can form a basis for $\mathcal{F}_N$

# Hartree-Fock Variational Approximation

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i, p_i) \; + \; \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{N} w(r_i, r_j)$$

seek the variational minimum of the energy expectation value among Fermionic wfcs given by a **single Slater determinant**

$$E^{HF} = \min_{\Phi^{\{S\}}=\mathcal{A}[\phi_1\cdots\phi_N]} \frac{\langle\Phi^{\{S\}}|\mathcal{H}_{el}|\Phi^{\{S\}}\rangle}{\langle\Phi^{\{S\}}|\Phi^{\{S\}}\rangle}$$

The variational parameters are the single particle orbitals

NB: the variational space is not a subspace

# Hartree-Fock Energy

$$E_{GS}^{HF} = \min_{\Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \;\geq\; E_{GS}$$

$$E_{GS} = E_{GS}^{HF} + E_{corr}, \qquad E_{corr} \leq 0$$

Chemist definition of correlation: whatever is beyond HF

Probability to find one particle in r  (and one in r')

$$\langle \Phi^{\{H\}} | \delta(r_1 - r) | \Phi^{\{H\}} \rangle = |\phi_1(r)|^2$$

$$\langle \Phi^{\{H\}} | \delta(r_1 - r)\delta(r_2 - r') | \Phi^{\{H\}} \rangle = |\phi_1(r)|^2 |\phi_2(r')|^2$$

# Hartree-Fock Energy

$$E_{GS}^{HF} = \min_{\Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \;\geq\; E_{GS}$$

$$E_{GS} = E_{GS}^{HF} + E_{corr}, \qquad E_{corr} \leq 0$$

Chemist definition of correlation: whatever is beyond HF

Probability to find one particle in r (and one in r')

$$\langle \Phi^{\{S\}} | \delta(r_1 - r) | \Phi^{\{S\}} \rangle = n(r)/N$$

$$\langle \Phi^{\{S\}} | \delta(r_1 - r)\delta(r_2 - r') | \Phi^{\{S\}} \rangle = \frac{n(r)n(r') - |\gamma(r, r')|^2}{N(N-1)}$$

# Hartree-Fock Energy Functional

$$E^{HF}[\Phi^{\{S\}}] \;=\sum_i \langle\phi_i| - \frac{\hbar^2}{2m}\nabla^2|\phi_i\rangle + \int v_{ext}(r)n(r)\,dr$$

**Hartree energy**
$E_H > 0$

$$+\,\frac{1}{2}\sum_{i,j}^{N}\int |\phi_i(r)|^2\;\frac{e^2}{|r-r'|}\;|\phi_j(r')|^2\;drdr'$$

**Exchange (Fock) energy**
$E_x < 0$

$$-\,\frac{1}{2}\sum_{i,j}^{N}\int \phi_i^*(r)\phi_j(r)\;\frac{e^2}{|r-r'|}\;\phi_j^*(r')\phi_i(r')\,drdr'$$

*orthogonality conditions*

$$-\sum_{i,j}^{N}\Lambda_{i,j}\left(\langle\phi_i|\phi_j\rangle-\delta_{ij}\right)$$

$\delta\; E^{HF}[\Phi^{\{S\}}]=0$ leads to the **Hartree-Fock eqs**

# Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + \sum_j^N \int |\phi_j(r')|^2 \frac{e^2}{|r-r'|} dr'\right] \phi_i(r)$$

$$-\sum_j^N \int \phi_j(r) \frac{e^2}{|r-r'|} \phi_j^*(r')\phi_i(r') dr' = \sum_j \Lambda_{i,j}\phi_j(r)$$

# Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2\int \frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)$$

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# Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2\int\frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)$$

$$- e^2\int\frac{\gamma(r,r')}{|r-r'|}\phi_i(r')dr' = \sum_j \Lambda_{i,j}\phi_j(r)$$

# Hartree-Fock equations

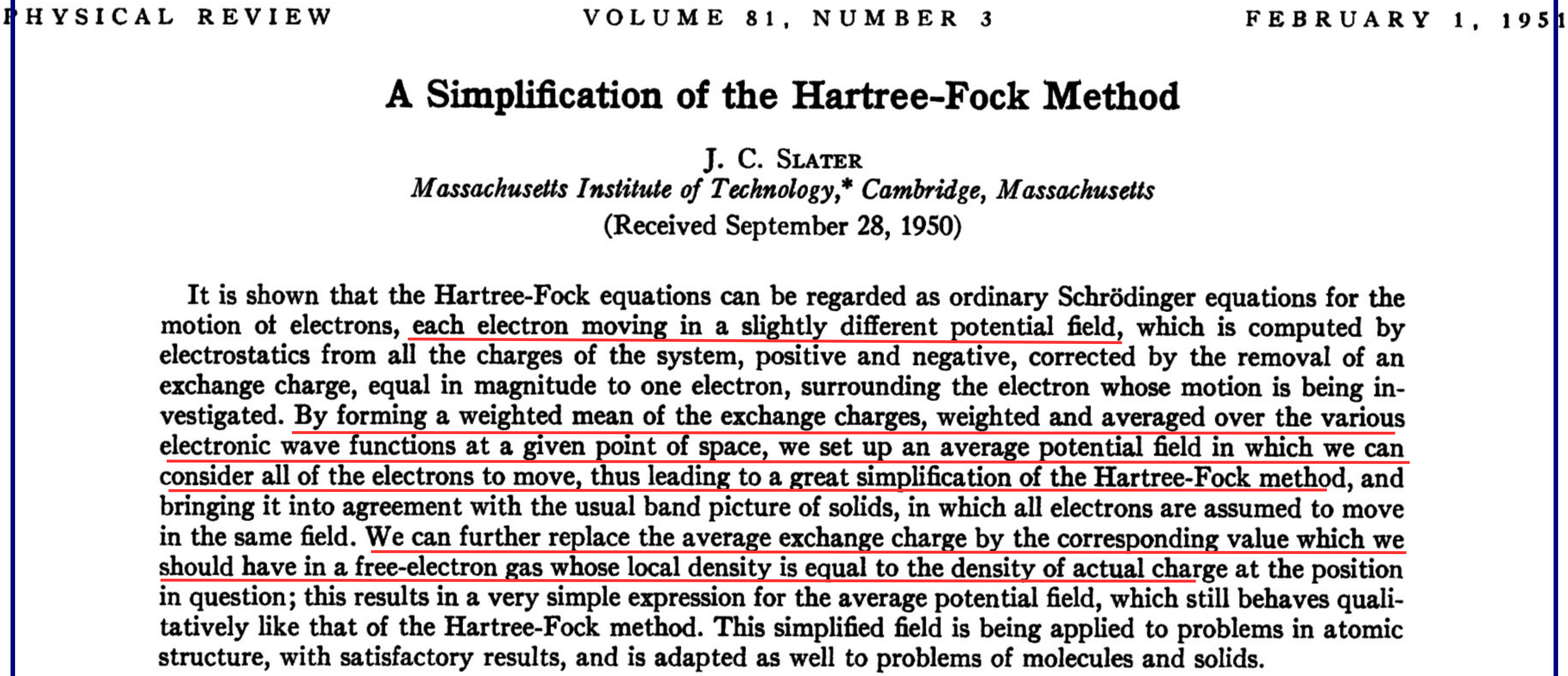
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2\int\frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)$$

$$-\,e^2\int\frac{\gamma(r,r')}{|r-r'|}\phi_i(r')dr' = \varepsilon_i\,\phi_i(r)$$

independent electrons in a self-consistent potential

$$V_{scf}(r) = V_{ext}(r) + e^2\int\frac{n(r')}{|r-r'|}dr' + \hat{V}_x$$

non-local exchange (Fock) operator



PHYSICAL REVIEW VOLUME 81, NUMBER 3 FEBRUARY 1, 1951

# A Simplification of the Hartree-Fock Method

J. C. SLATER
*Massachusetts Institute of Technology,* Cambridge, Massachusetts*

(Received September 28, 1950)

It is shown that the Hartree-Fock equations can be regarded as ordinary Schrödinger equations for the motion of electrons, each electron moving in a slightly different potential field, which is computed by electrostatics from all the charges of the system, positive and negative, corrected by the removal of an exchange charge, equal in magnitude to one electron, surrounding the electron whose motion is being investigated. By forming a weighted mean of the exchange charges, weighted and averaged over the various electronic wave functions at a given point of space, we set up an average potential field in which we can consider all of the electrons to move, thus leading to a great simplification of the Hartree-Fock method, and bringing it into agreement with the usual band picture of solids, in which all electrons are assumed to move in the same field. We can further replace the average exchange charge by the corresponding value which we should have in a free-electron gas whose local density is equal to the density of actual charge at the position in question; this results in a very simple expression for the average potential field, which still behaves qualitatively like that of the Hartree-Fock method. This simplified field is being applied to problems in atomic structure, with satisfactory results, and is adapted as well to problems of molecules and solids.

# Local approximations for Vx

independent electrons in a self-consistent potential

$$V_{scf}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r - r'|} dr' + \hat{V}_x$$

non-local exchange (Fock) operator

$$\hat{V}_x \phi_i(r) = -\, e^2 \int \frac{\gamma(r, r')}{|r - r'|} \phi_i(r') dr'$$

local approximations:

*Slater Potential*

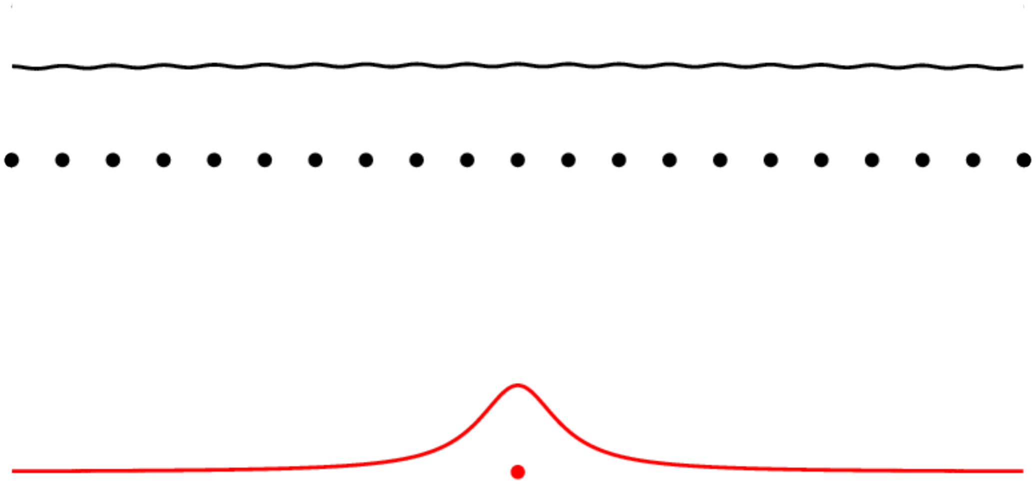
$$v_x^{SLA}(r) \;=\; \frac{1}{n(r)} \sum_i \phi_i^*(r) \hat{V}_x \phi_i(r)$$

statistical average

Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951)

When computed for the HEG and then applied locally it gives the $X_\alpha$ method

# Homogeneous Electron Gas



Consider a periodic system of electrons and ions (neutral)

and let's smear the ionic charge distribution

the external potential tends to a constant (-infinity)

# Hartree-Fock in the HEG

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} \frac{p_i^2}{2m_e} + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^{N} \frac{e^2}{|r_i - r_j|} - \sum_{i}^{N} \int \rho_{ion}(r') \frac{e^2}{|r' - r_i|}\, dr'$$

$$+\frac{1}{2}\int \rho_{ion}(r) \frac{e^2}{|r - r'|} \rho_{ion}(r')\, dr dr'$$

In the Jellium model (homogeneous electron gas) the ionic density is *uniform* and the system is *neutral*

$$\rho_{ion}(r) = n = \frac{N}{V}$$

The system is translational invariant w/o ext magnetic field
It is *postulated* that so is the HF scf hamiltonian (to be verif).
HF wfcs are therefore just plane waves.

$$\psi_{k,\sigma}(r) = \frac{1}{\sqrt{V}} e^{+ikr} |\sigma\rangle$$

# Hartree-Fock in the HEG

The system is translational invariant w/o ext magnetic field
It is *postulated* that so is the HF scf hamiltonian (to be verif).
HF wfcs are therefore just plane waves.

$$\psi_{k,\sigma}(r) = \frac{1}{\sqrt{V}} e^{+ikr} |\sigma\rangle$$

The density is uniform

$$\rho_{el}(r) = \sum_{\sigma} \sum_{|k|<k_F} |\psi_{k,\sigma}(r)|^2 = \frac{2}{V} \sum_{|k|<k_F} 1 \qquad \sum_{k} \to \frac{V}{(2\pi)^3} \int d^3k$$

$$= \frac{V}{(2\pi)^3} \frac{2}{V} \int_{|k|<k_F} d^3k = \frac{2}{(2\pi)^3} 4\pi \int_0^{k_F} k^2 dk = \frac{k_F^3}{3\pi^2} \underset{\substack{\uparrow \\ \text{neutrality}}}{=} n$$

$$\rho_{\uparrow}(r) = \rho_{\downarrow}(r) = \frac{n}{2} \longleftarrow \text{non magnetic sol.}$$

# Hartree-Fock in the HEG

$$\rho_{el}(r) = \rho_{ion}(r) = n$$

The total electrostatic energy of jellium is zero

$$E_{tot.e.s.} = E_H + E_{el-ion} + E_{ion-ion}$$

$$E_{tot.e.s.} =$$

$$\frac{e^2}{2}\int \frac{\rho_{el}(r)\rho_{el}(r')}{|r-r'|}drdr' - e^2\int \frac{\rho_{el}(r)\rho_{ion}(r')}{|r-r'|}drdr' + \frac{e^2}{2}\int \frac{\rho_{ion}(r)\rho_{ion}(r')}{|r-r'|}drdr'$$

$$= \frac{e^2}{2}\int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r-r'|}drdr' = 0$$

# Hartree-Fock in the HEG

In general ...

$$E_{tot.e.s.} = \frac{e^2}{2}\int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r-r'|} dr dr'$$

$$\nabla \cdot \mathbf{E}(r) = e\,\rho_{tot}(r), \qquad \nabla^2 \frac{1}{|r-r'|} = -4\pi\,\delta(r-r')$$

$$E_{tot.e.s.} = \frac{1}{8\pi}\int |\mathbf{E}(r)|^2 dr$$

$$\rho_{tot}(r) = 0 \quad \Longrightarrow \quad \nabla \cdot \mathbf{E}(r) = 0 \quad \Longrightarrow \quad \mathbf{E}(r) = const$$

in metals the field is completely screened

no macroscopic electric field in insulating samples

# Hartree-Fock in the HEG

$$E_{tot.e.s.} = E_H + E_{el-ion} + E_{ion-ion} = 0$$

For the same reason

$$V_{tot.e.s.}(r) = V_{ion}(r) + V_H(r)$$

$$= -e^2 \int \frac{\rho_{ion}(r')}{|r-r'|} dr' + e^2 \int \frac{\rho_{el}(r')}{|r-r'|} dr' = e^2 \int \frac{\rho_{tot}(r')}{|r-r'|} dr' = 0$$

The average value of the electrostatic potential is actually *arbitrary* and is *conventionally* set to zero.

There is no simple way to compare the eigenvalues of two different periodic calculations.

# Hartree-Fock in the HEG

Exchange potential:

$$V_x\psi_{k\sigma}(r) = -\sum_{\sigma'}\sum_{k'}\psi_{k'\sigma'}(r)\int \psi^*_{k'\sigma'}\underbrace{(r')\frac{e^2}{|r-r'|}\psi_{k\sigma}}_{\delta_{\sigma\sigma'}}(r)d^3r'$$

$$= -\sum_{|k'|<k_F}\frac{1}{V^{\frac{3}{2}}}e^{+ik'r}\int e^{-i(k'-k)r'}\frac{e^2}{|r-r'|}d^3r'\;|\sigma\rangle$$

$$= \left[-\sum_{|k'|<k_F}\frac{1}{V}\int e^{-i(k'-k)(r'-r)}\frac{e^2}{|r-r'|}d^3r'\right]\frac{e^{+ikr}}{\sqrt{V}}|\sigma\rangle$$

# Hartree-Fock in the HEG

Exchange potential:

$$V_x\psi_{k\sigma}(r) = \left[-\sum_{|k'|<k_F}\frac{1}{V}\int e^{-i(k'-k)(r'-r)}\frac{e^2}{|r-r'|}d^3r'\right]\psi_{k\sigma}(r)$$

$$= \underbrace{\left[-\sum_{|k'|<k_F} V(k-k')\right]}_{\text{a  k-dependent constant}}\psi_{k\sigma}(r)$$

where $$V(q) = \frac{1}{V}\int\frac{e^2}{|r|}e^{-iqr}d^3r = \frac{1}{V}\frac{4\pi e^2}{q^2}$$

# Hartree-Fock in the HEG

Exchange potential:

$$V_x \psi_{k\sigma}(r) = \left[ - \sum_{|k'|<k_F} V(k-k') \right] \psi_{k\sigma}(r)$$

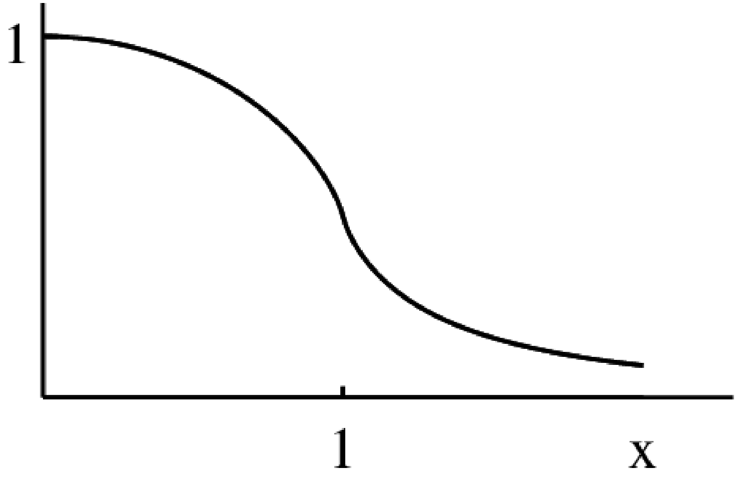
This integral is done, for instance, in Kittel "QTofS"

$$\frac{1}{V} \sum_{|k'|<k_F} \frac{4\pi e^2}{|k-k'|^2} = \frac{1}{(2\pi)^3} \int_{|k'|<k_F} d^3k' \frac{4\pi e^2}{|k-k'|^2} = \frac{2e^2}{\pi} k_F F(k/k_F)$$

Where $F$ is the Lindhard function

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

$$F(0) = 1, \quad F(1) = 1/2,$$
$$F'(1) = -\infty$$

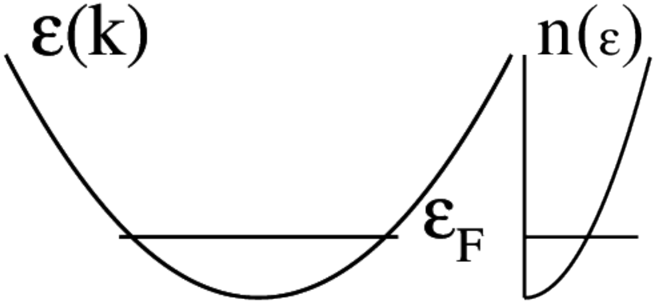


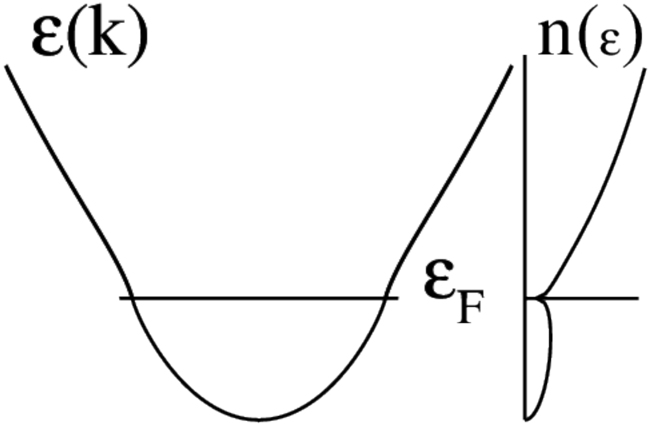
# Hartree-Fock in the HEG

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{\pi}k_F F(k/k_F)\right]\psi_{k\sigma}(r) = \varepsilon_{k\sigma}\psi_{k\sigma}(r)$$

$$\varepsilon_{k\sigma} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi}k_F F(k/k_F)$$

$$k_F = \left(3\pi^2 n\right)^{1/3}$$





for $n \longrightarrow \infty$

kinetic energy dominates

at any finite density *n*

$n(\varepsilon_F) = 0$

# Slater approximation for Vx

In the HEG the exch. potential is a simple function of *n* (and *k*)

$$V_x(k,\sigma) = -\frac{2e^2}{\pi} k_F F(k/k_F) = -4e^2 \left(\frac{3\, n_\sigma}{4\pi}\right)^{1/3} F(k/k_F)$$

Slater approx is to apply it locally with some effective *F*

$$V_x(r,\sigma) = -4e^2 \left(\frac{3\, n_\sigma(r)}{4\pi}\right)^{1/3} \tilde{F}$$

*1) average over the occupied states*

$$\tilde{F} = \langle F \rangle = \frac{3}{4\pi}\int_{|x|<1} F(x) d^3x \; = \; 3\int_0^1 x^2 F(x) dx = 3/4$$

$$V_x(r,\sigma) = -3e^2 \left(\frac{3\, n_\sigma(r)}{4\pi}\right)^{1/3}$$

*2) value good for the Fermi energy*

$$\tilde{F} = F(k_F/k_F) = 1/2$$

$$V_x(r,\sigma) = -2e^2 \left(\frac{3\, n_\sigma(r)}{4\pi}\right)^{1/3}$$

# Slater approximation for Vx

In the HEG the exch. potential is a simple function of *n* (and *k*)

$$V_x(k,\sigma) = -\frac{2e^2}{\pi} k_F F(k/k_F) = -4e^2 \left(\frac{3\,n_\sigma}{4\pi}\right)^{1/3} F(k/k_F)$$

Slater approx is to apply it locally with some effective *F*

$$V_x(r,\sigma) = -4e^2 \left(\frac{3\,n_\sigma(r)}{4\pi}\right)^{1/3} \tilde{F} \qquad \text{with} \qquad \frac{1}{2} < \tilde{F} < \frac{3}{4}$$

or $$V_x(r,\sigma) = -3e^2\,\alpha \left(\frac{3\,n_\sigma(r)}{4\pi}\right)^{1/3} \qquad \text{with} \qquad \frac{2}{3} < \alpha < 1$$

In the $X_\alpha$ method $\alpha$ is used as a parameter to generate orbitals to be used in the HF energy evaluation

# Local approximations for Vx

independent electrons in a self-consistent potential

$$V_{scf}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r-r'|} dr' + \hat{V}_x$$

non-local exchange (Fock) operator

$$\hat{V}_x \phi_i(r) = -\, e^2 \int \frac{\gamma(r,r')}{|r-r'|} \phi_i(r') dr'$$

local approximations:

*Slater Potential*

$$v_x^{SLA}(r) \;=\; \frac{1}{n(r)} \sum_i \phi_i^*(r) \hat{V}_x \phi_i(r)$$

statistical average

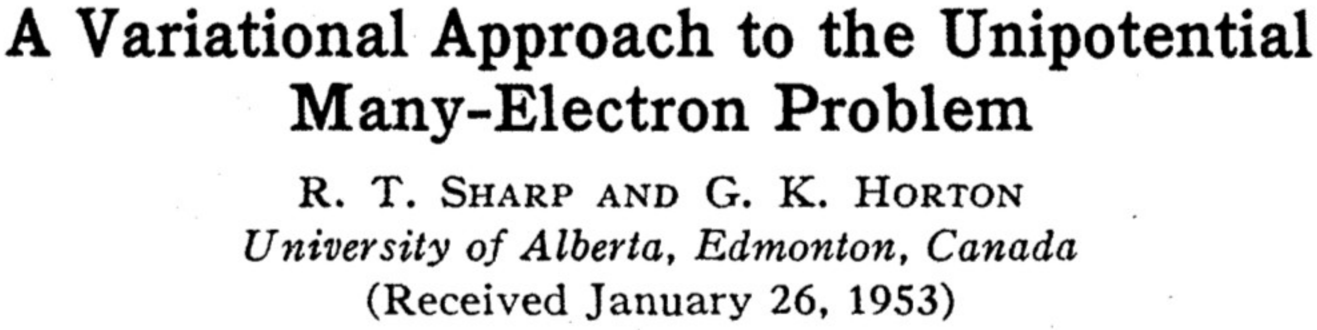
Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951)

*Optimized Effective Potential*

$v_x^{OEP}(r)$ : The best local potential in a variational sense

Sharp and Horton, Phys. Rev. 90, 317 (1953)
Talman and Shadwick, Phys. Rev. A 14, 36 (1976)

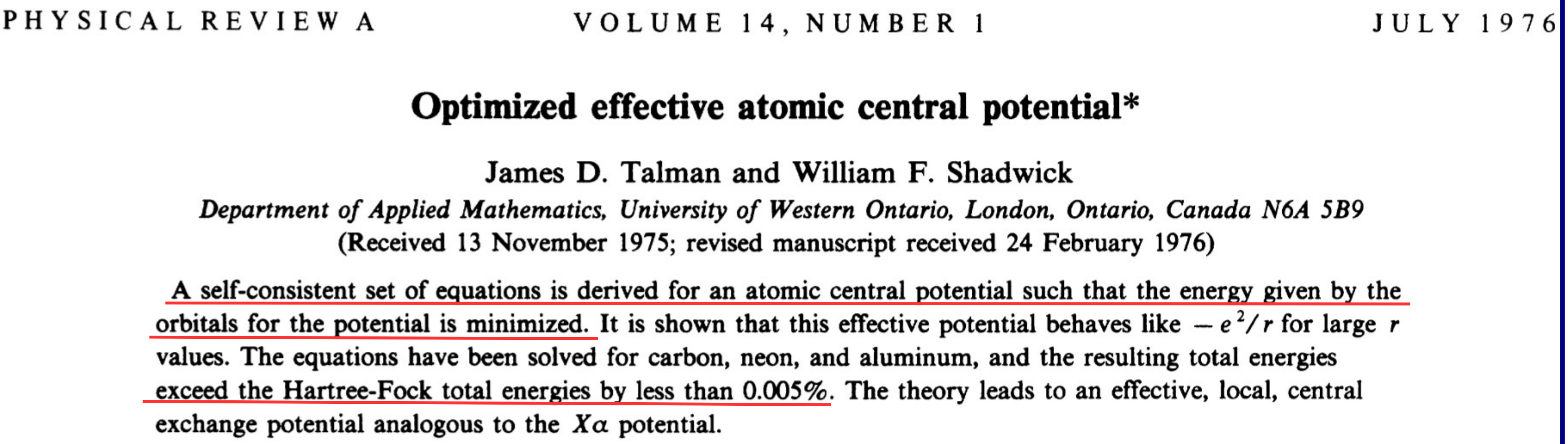
Physical Review **90**, 317 (1953)



# A Variational Approach to the Unipotential Many-Electron Problem

R. T. SHARP AND G. K. HORTON
*University of Alberta, Edmonton, Canada*

(Received January 26, 1953)



PHYSICAL REVIEW A VOLUME 14, NUMBER 1 JULY 1976

# Optimized effective atomic central potential*

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(Received 13 November 1975; revised manuscript received 24 February 1976)

A self-consistent set of equations is derived for an atomic central potential such that the energy given by the orbitals for the potential is minimized. It is shown that this effective potential behaves like $-e^2/r$ for large $r$ values. The equations have been solved for carbon, neon, and aluminum, and the resulting total energies exceed the Hartree-Fock total energies by less than 0.005%. The theory leads to an effective, local, central exchange potential analogous to the $X\alpha$ potential.

# OEP Variational Approximation

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i, p_i) \; + \; \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^{N} w(r_i, r_j)$$

seek the variational minimum of the energy expectation value among Fermionic wfcs given by a **single Slater determinant of a *local* potential**

$$E^{OEP} = \min_{V \to \Phi^{\{S\}}} \frac{\langle \Phi^{\{S\}} | \mathcal{H}_{el} | \Phi^{\{S\}} \rangle}{\langle \Phi^{\{S\}} | \Phi^{\{S\}} \rangle}$$

The variational parameters determine the local potential

# OEP vs Hartree-Fock Energy

$$E_{GS}^{HF} = \min_{\Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \ \geq \ E_{GS}$$

$$E_{GS} = E_{GS}^{HF} + E_{corr}, \qquad E_{corr} \leq 0$$

Chemist definition of correlation: whatever is beyond HF

$$E_{GS}^{OEP} = \min_{V \to \Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \ \geq E_{GS}^{HF} \geq \ E_{GS}$$

DFT definition of correlation: what is beyond OEP (aka EXX)

numerically $\quad E_{GS}^{OEP} \approx E_{GS}^{HF}$

conceptually $\quad E_{GS}^{OEP} \neq E_{GS}^{HF}$

# OEP Energy Functional

$$E^{OEP}[v_{eff}] = \sum_i \langle \phi_i | -\frac{\hbar^2}{2m}\nabla^2 | \phi_i \rangle + \int v_{ext}(\mathbf{r}) n(\mathbf{r})\, d\mathbf{r}$$

**Hartree energy**
$E_H > 0$

$$+\frac{1}{2}\sum_{i,j}^{N}\int |\phi_i(\mathbf{r})|^2 \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \, |\phi_j(\mathbf{r}')|^2 \, d\mathbf{r}d\mathbf{r}'$$

**Exchange (Fock) energy**
$E_x < 0$

$$-\frac{1}{2}\sum_{i,j}^{N}\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \, \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$$

such that $$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad i = 1, \ldots, N$$

$\delta\, E^{OEP}[v_{eff}] = 0$ leads to the **OEP eqs** for $v_{eff}$

# OEP equations

$$0 \;=\; 2\Re \sum_i^{occ} \langle\phi_i| -\frac{\hbar^2}{2m}\nabla^2 + v_{ext} + V_H + \hat{V}_x \, |\delta\phi_i\rangle, \quad \forall \delta v_{eff}$$

such that $\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff} - \varepsilon_i\right] |\phi_i\rangle = 0, \quad i = 1, ..., N$

and $\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff} - \varepsilon_i\right] |\delta\phi_i\rangle = -P_c \, \delta v_{eff} |\phi_i\rangle$

Let $v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + v_x(\mathbf{r})$

$$0 \;=\; 2\Re \sum_i^{occ} \langle\phi_i|\hat{V}_x - v_x \, |\delta\phi_i\rangle, \quad \forall \delta v_{eff}$$

$$0 \;=\; 2\Re \sum_i^{occ} \sum_{j\neq i} \frac{\langle\phi_i|\hat{V}_x - v_x \, |\phi_j\rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r})\phi_i(\mathbf{r})$$

# OEP equations

$$0 \;=\; 2\Re \sum_{i}^{occ} \sum_{j\neq i} \frac{\langle \phi_i | \hat{V}_x - v_x \; | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r})\phi_i(\mathbf{r})$$

$$\int \chi_0(\mathbf{r},\mathbf{r}')\; v_x(\mathbf{r}')\; d\mathbf{r}' \;=\; 2\Re \sum_{i}^{occ} \sum_{j\neq i} \frac{\langle \phi_i | \hat{V}_x \; | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r})\phi_i(\mathbf{r})$$

with
$$\chi_0(\mathbf{r},\mathbf{r}') = 2\Re \sum_{i}^{occ} \sum_{j\neq i} \frac{\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_j}$$

# OEP equations

$$0 \;=\; 2\Re \sum_{i}^{occ} \sum_{j}^{empty} \frac{\langle \phi_i | \hat{V}_x - v_x \, | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r})$$

$$\int \chi_0(\mathbf{r}, \mathbf{r}') \; v_x(\mathbf{r}') \; d\mathbf{r}' \;=\; 2\Re \sum_{i}^{occ} \sum_{j}^{empty} \frac{\langle \phi_i | \hat{V}_x \, | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r})$$

with

$$\chi_0(\mathbf{r}, \mathbf{r}') = 2\Re \sum_{i}^{occ} \sum_{j}^{empty} \frac{\phi_i^*(\mathbf{r}') \phi_j(\mathbf{r}') \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_j}$$

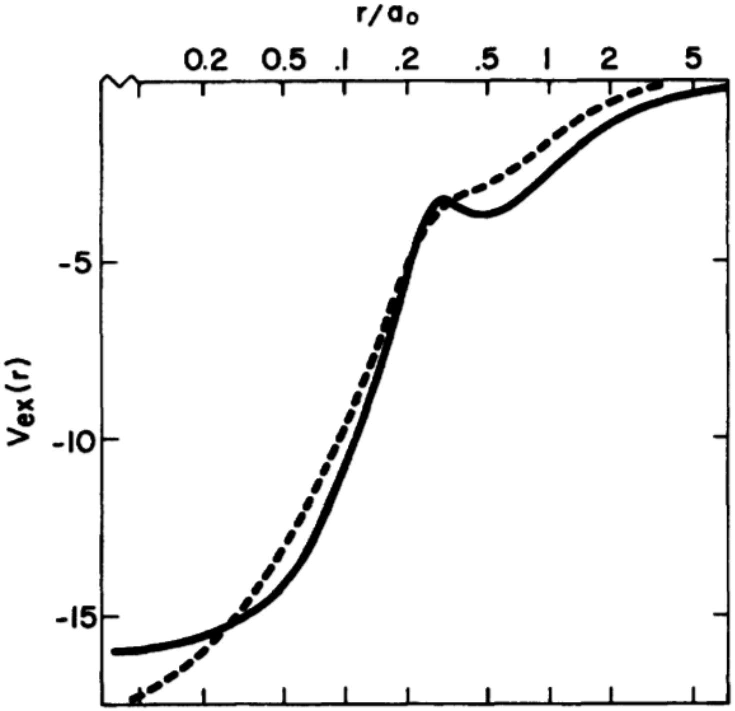

FIG. 2. Optimized effective exchange potential, solid curve, and the $X\alpha$ exchange potential, broken curve, for neon.

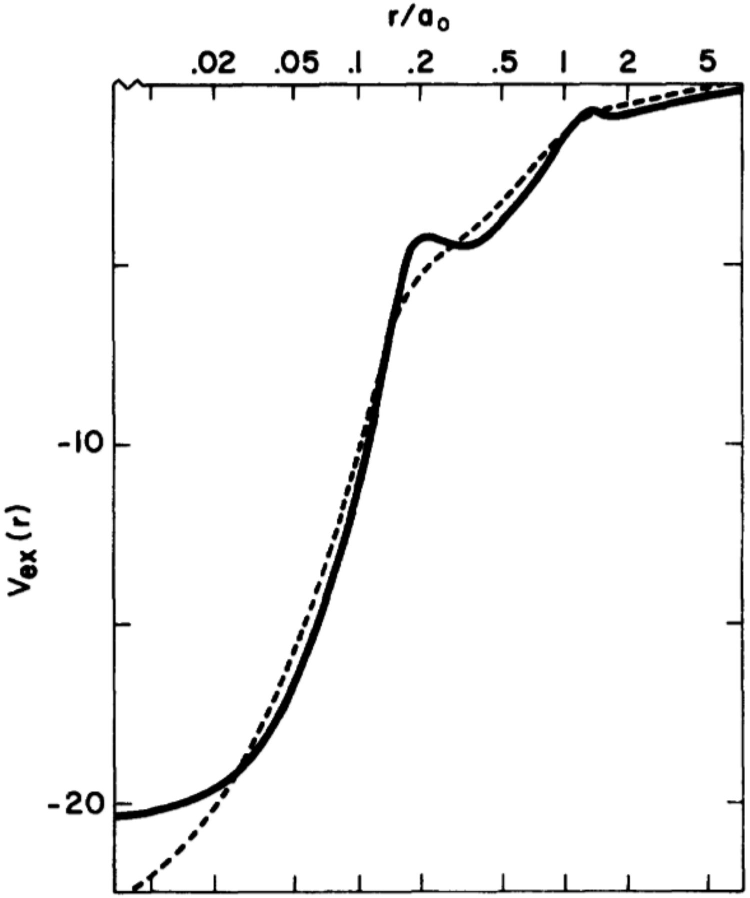

FIG. 3. Optimized effective exchange potential, solid curve, and the $X\alpha$ exchange potential, broken curve, for aluminum.

MR Norman & DD Koelling *Phys Rev B* **30**,5530 (1984)

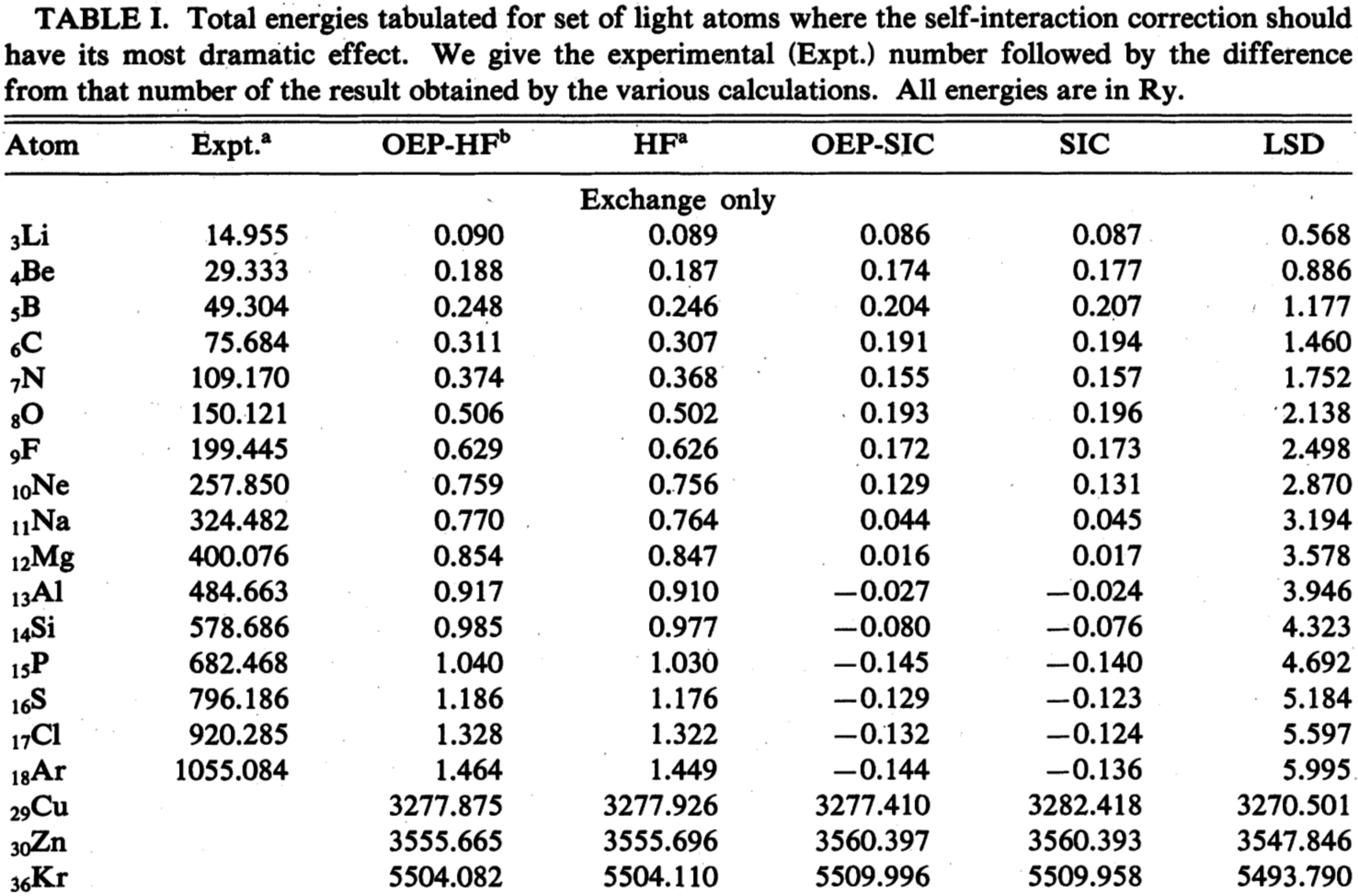

TABLE I. Total energies tabulated for set of light atoms where the self-interaction correction should have its most dramatic effect. We give the experimental (Expt.) number followed by the difference from that number of the result obtained by the various calculations. All energies are in Ry.

| Atom | Expt.[a] | OEP-HF[b] | HF[a] | OEP-SIC | SIC | LSD |
|---|---|---|---|---|---|---|
| | | | Exchange only | | | |
| ${}_{3}$Li | 14.955 | 0.090 | 0.089 | 0.086 | 0.087 | 0.568 |
| ${}_{4}$Be | 29.333 | 0.188 | 0.187 | 0.174 | 0.177 | 0.886 |
| ${}_{5}$B | 49.304 | 0.248 | 0.246 | 0.204 | 0.207 | 1.177 |
| ${}_{6}$C | 75.684 | 0.311 | 0.307 | 0.191 | 0.194 | 1.460 |
| ${}_{7}$N | 109.170 | 0.374 | 0.368 | 0.155 | 0.157 | 1.752 |
| ${}_{8}$O | 150.121 | 0.506 | 0.502 | 0.193 | 0.196 | 2.138 |
| ${}_{9}$F | 199.445 | 0.629 | 0.626 | 0.172 | 0.173 | 2.498 |
| ${}_{10}$Ne | 257.850 | 0.759 | 0.756 | 0.129 | 0.131 | 2.870 |
| ${}_{11}$Na | 324.482 | 0.770 | 0.764 | 0.044 | 0.045 | 3.194 |
| ${}_{12}$Mg | 400.076 | 0.854 | 0.847 | 0.016 | 0.017 | 3.578 |
| ${}_{13}$Al | 484.663 | 0.917 | 0.910 | −0.027 | −0.024 | 3.946 |
| ${}_{14}$Si | 578.686 | 0.985 | 0.977 | −0.080 | −0.076 | 4.323 |
| ${}_{15}$P | 682.468 | 1.040 | 1.030 | −0.145 | −0.140 | 4.692 |
| ${}_{16}$S | 796.186 | 1.186 | 1.176 | −0.129 | −0.123 | 5.184 |
| ${}_{17}$Cl | 920.285 | 1.328 | 1.322 | −0.132 | −0.124 | 5.597 |
| ${}_{18}$Ar | 1055.084 | 1.464 | 1.449 | −0.144 | −0.136 | 5.995 |
| ${}_{29}$Cu | | 3277.875 | 3277.926 | 3277.410 | 3282.418 | 3270.501 |
| ${}_{30}$Zn | | 3555.665 | 3555.696 | 3560.397 | 3560.393 | 3547.846 |
| ${}_{36}$Kr | | 5504.082 | 5504.110 | 5509.996 | 5509.958 | 5493.790 |

# Density Functional Perturbation Theory

# and

# Response Functions

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# Total KS energy

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

# KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

# KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

# KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

# KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

$$\begin{tikzcd} V_{KS}(r) \arrow[r] & \varphi_i(r) \arrow[r] & \rho(r) \arrow[ll, bend left] \end{tikzcd}$$

# Total KS energy

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

## Total KS energy

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

## Hellmann-Feynman Theorem

$$F_{I\alpha} = -\frac{\partial E_{el+ion}}{\partial R_{I\alpha}} = -\int \frac{\partial V_{ext}(r)}{\partial R_{I\alpha}}\rho(r)dr \; - \; \frac{\partial E_{WLD}}{\partial R_{I\alpha}}$$

$$\frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial \lambda}$$

the linear variation of the GS density is not needed

# KS energy expansion

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

$$\frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial \lambda}$$

# KS energy expansion

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H\lfloor\rho\rceil + E_{xc}\lfloor\rho\rceil + E_{WLD}$$

$$\frac{\partial E_{el+ion}}{\partial\lambda} = \int \frac{\partial V_{ext}(r)}{\partial\lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial\lambda}$$

$$\frac{\partial^2 E_{el+ion}}{\partial\lambda\partial\mu} = \int \frac{\partial^2 V_{ext}(r)}{\partial\lambda\partial\mu}\rho(r)dr + \int \frac{\partial V_{ext}(r)}{\partial\lambda}\frac{\partial\rho(r)}{\partial\mu}dr + \frac{\partial^2 E_{WLD}}{\partial\lambda\partial\mu}$$

the linear variation of the GS density is needed

# static density response

$$\Delta\rho(r) = \int \chi(r,r')\, \Delta V_{ext}(r')\, dr'$$

Interacting electron density-density response function

$$\Delta\rho(r) = \int \chi_0(r,r')\, \Delta V_{KS}(r')\, dr'$$

Non-interacting electron density-density response function

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2 \int \frac{\Delta\rho(r')}{|r-r'|} dr' + \int \frac{\delta v_{xc}(r)}{\delta\rho(r')} \Delta\rho(r') dr'$$

$$\chi = \chi_0 + \chi_0 (v_c + f_{xc}) \chi$$ Dyson-like equation

Random Phase Approximation $f_{xc} = 0$

# non-interacting response function

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$V_{KS} \to V_{KS} + \delta V_{KS}, \;\; \phi_i \to \phi_i + \delta\phi_i, \;\; n(r) \to n(r) + \delta n(r)$$

$$\delta n(r) = \sum_i^{occ} \phi_i^*(r)\; \delta\phi_i(r) + c.c., \qquad \delta\phi_i(r) = \sum_{j\neq i} \phi_j(r) \frac{\langle\phi_j|\delta V_{KS}|\phi_i\rangle}{\varepsilon_i - \varepsilon_j}$$

$$\chi_0(\mathbf{r},\mathbf{r}') = 2\sum_i^{occ} \sum_j^{empty} \frac{\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_j}$$

# KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

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# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\varphi_i(r) = -\left(\Delta V_{KS} - \Delta\varepsilon_i\right)\varphi_i(r)$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\varphi_i(r) = -\left(\Delta V_{KS} - \Delta\varepsilon_i\right)\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\varphi_i(r)$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right] \Delta\tilde{\varphi}_i(r) = -P_c\, \Delta V_{KS}(r)\, \varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\, \Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + \Delta V_H(r) + \Delta v_{xc}(r)$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int\frac{\delta v_{xc}(r)}{\delta\rho(r')}\Delta\rho(r')dr'$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

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$$\begin{tikzcd}\Delta V_{KS} \arrow[r] & \Delta\tilde{\varphi}_i(r) \arrow[r] & \Delta\rho(r) \arrow[ll, bend left]\end{tikzcd}$$

# DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int f_{xc}\Delta\rho(r')dr'$$

$$\begin{tikzcd} \Delta V_{KS} \arrow[r] & \Delta\tilde{\varphi}_i(r) \arrow[r] & \Delta\rho(r) \arrow[ll, bend left] \end{tikzcd}$$

## Evaluate second order derivatives

$$\frac{\partial^2 E_{el+ion}}{\partial\lambda\partial\mu} = \int\frac{\partial^2 V_{ext}(r)}{\partial\lambda\partial\mu}\rho(r)dr + \int\frac{\partial V_{ext}(r)}{\partial\lambda}\frac{\partial\rho(r)}{\partial\mu}dr + \frac{\partial^2 E_{WLD}}{\partial\lambda\partial\mu}$$

PHYSICAL REVIEW A VOLUME 45, NUMBER 1 1 JANUARY 1992

# Construction and application of an accurate local spin-polarized Kohn-Sham potential with integer discontinuity: Exchange-only theory

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(Received 25 April 1991)

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PHYSICAL REVIEW A VOLUME 46, NUMBER 9 1 NOVEMBER 1992

# Systematic approximations to the optimized effective potential: Application to orbital-density-functional theory

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PHYSICAL REVIEW A VOLUME 47, NUMBER 1 JANUARY 1993

# Self-consistent calculations of atomic properties using self-interaction-free exchange-only Kohn-Sham potentials

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(Received 1 May 1992)

# KLI equations

$$0 \;=\; 2\Re \sum_{i}^{occ} \sum_{j\neq i} \frac{\langle \phi_i | \hat{V}_x - v_x \, | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r})$$

$$\varepsilon_j - \varepsilon_i \approx \alpha \qquad G(\mathbf{r}, \mathbf{r}', \varepsilon_i) = \sum_{j\neq i} \frac{\phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_i}$$

$$\approx \frac{1}{\alpha} \left[ \delta(\mathbf{r} - \mathbf{r}') - \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') \right]$$

$$v_x(\mathbf{r}) = v_x^{SLA}(\mathbf{r}) + \sum_{i}^{occ} \frac{|\phi_i(\mathbf{r})|^2}{n(\mathbf{r})} \left( \overline{v}_{x,i} - \overline{V}_{x,i} \right)$$

$$\overline{v}_{x,i} = \int v_x(\mathbf{r}) |\phi_i(\mathbf{r})|^2 d\mathbf{r}, \qquad \overline{V}_{x,i} = \langle \phi_i | \hat{V}_x | \phi_i \rangle$$

# KLI equations

$$v_x(\mathbf{r}) = v_x^{SLA}(\mathbf{r}) + \sum_i^{occ} \frac{|\phi_i(\mathbf{r})|^2}{n(\mathbf{r})} \left(\overline{v}_{x,i} - \overline{V}_{x,i}\right)$$

$$\overline{v}_{x,i} = \int v_x(\mathbf{r})|\phi_i(\mathbf{r})|^2 d\mathbf{r}, \qquad \overline{V}_{x,i} = \langle \phi_i|\hat{V}_x|\phi_i\rangle$$

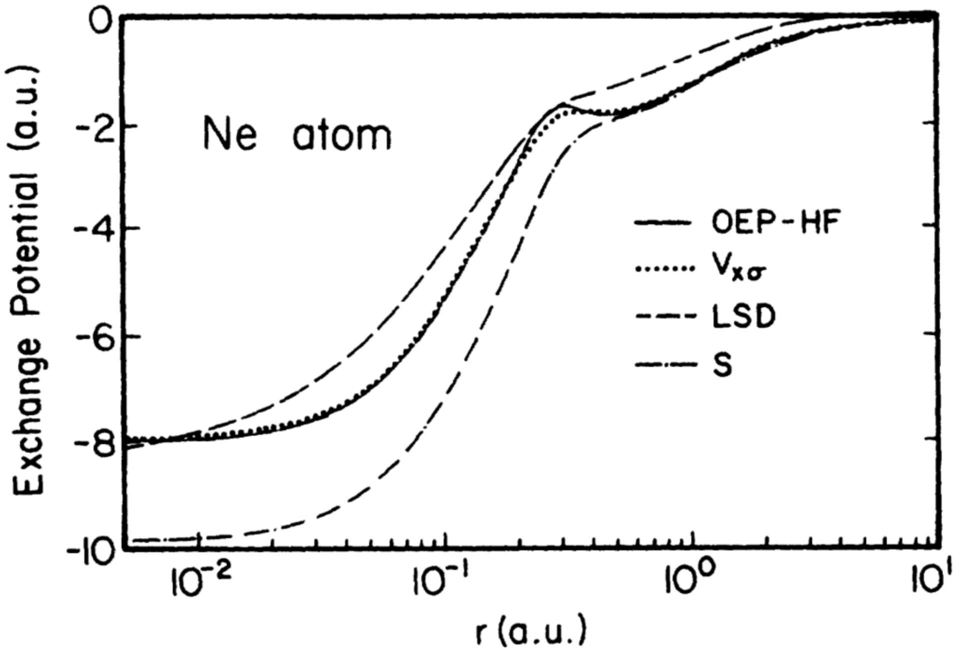
$$\overline{v}_{x,j} = \overline{v}_{x,j}^{SLA} + \sum_i^{occ} M_{i,j} \left(\overline{v}_{x,i} - \overline{V}_{x,i}\right)$$

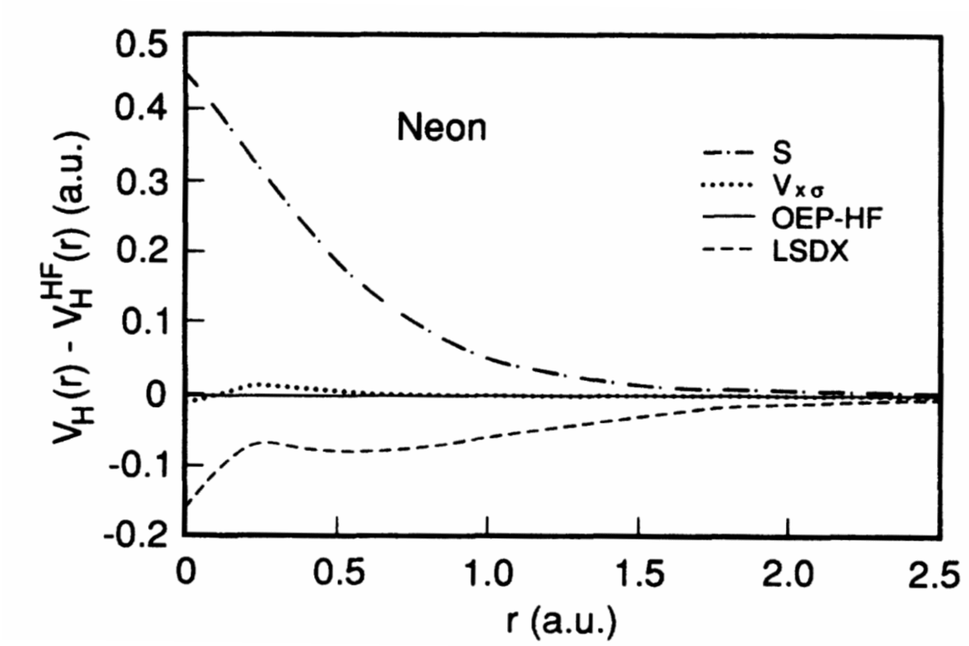
$$M_{i,j} = \int \frac{|\phi_i(\mathbf{r})|^2|\phi_j(\mathbf{r})|^2}{n(\mathbf{r})} d\mathbf{r}$$

$$\overline{v}_{x,j}^{SLA} = \int |\phi_j(\mathbf{r})|^2 v_x^{SLA}(\mathbf{r}) d\mathbf{r}$$

TABLE I. Comparison of overestimates of the OEP total energy $E^o$, calculated in various approximations compared with the overestimate of the Hartree-Fock total energy by $E^o$ (in mRy) for ten atoms with closed subshells. [$E_{\text{calc}}$ was calculated using $V_{x\sigma}$ given by Eq. (48).]

| Atom | $-E^{\text{HF}}$ (Ref. [22]) (Ry) | $E^o$ (Ref. [18]) $-E^{\text{HF}}$ | $E_{\text{calc}}-E^o$ | $E^{\text{HS}}$ (Ref. [21]) $-E^o$ | $E^{\text{LSD}}-E^o$ | $E^{\text{S}}-E^o$ |
|---|---|---|---|---|---|---|
| Be | 29.1460 | 1.1 | 0.3 | 2.0 | 8.7 | 22.1 |
| Ne | 257.0942 | 3.4 | 1.1 | 6.9 | 35.7 | 89.4 |
| Mg | 399.2292 | 6.0 | 1.8 | 10.6 | 28.5 | 157.2 |
| Ar | 1 053.6350 | 10.6 | 3.4 | 15.8 | 34.4 | 218.3 |
| Ca | 1 353.5164 | 12.6 | 4.4 | 18.6 | 32.2 | 291.5 |
| Zn | 3 555.6962 | 27.5 | 7.3 | 29.5 | 101.6 | 516.1 |
| Kr | 5 504.1100 | 24.1 | 6.3 | 26.9 | 64.3 | 574.0 |
| Sr | 6 263.0914 | 24.5 | 7.1 | 28.3 | 58.5 | 648.5 |
| Cd | 10 930.2662 | 37.4 | 12.0 | 43.4 | 88.7 | 837.8 |
| Xe | 14 464.2768 | 35.0 | 12.1 | 39.9 | 68.0 | 897.5 |





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