



**The Abdus Salam
International Centre for Theoretical Physics**



2137-10

**Joint ICTP-IAEA Advanced Workshop on Multi-Scale Modelling for
Characterization and Basic Understanding of Radiation Damage
Mechanisms in Materials**

12 - 23 April 2010

Electronic Structure Calculations

J.J. Kohanoff
*The Queen's University of Belfast
United Kingdom*

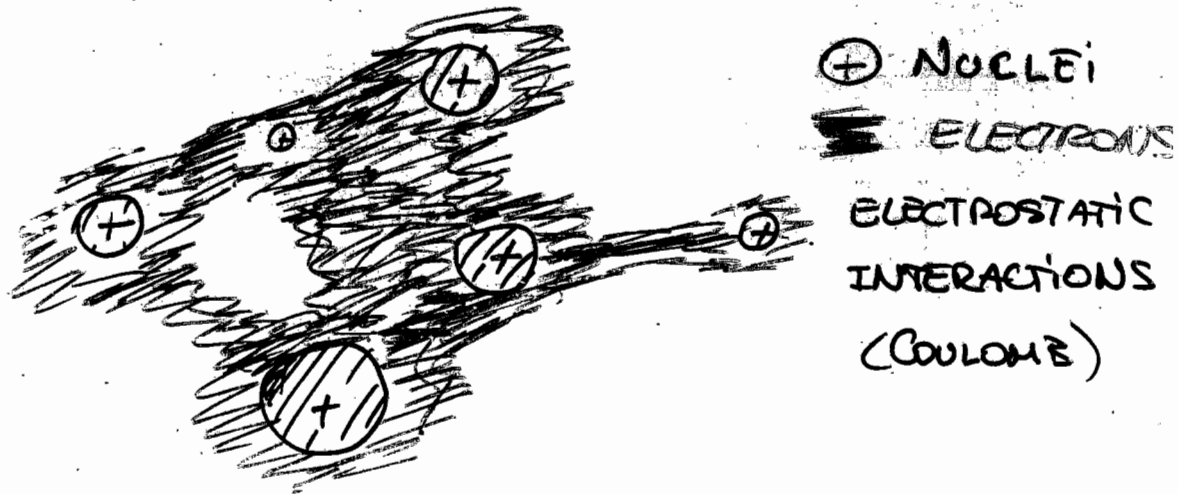
ELECTRONIC
STRUCTURE
CALCULATIONS

JORGE KOHANOFF
QUEEN'S UNIVERSITY BELFAST
U.K.

j.kohanoff@qub.ac.uk

LECTURE 1

The problem of the structure of matter



Hamiltonian of the Universe:

$$\begin{aligned}
 \hat{H} = & \underbrace{-\sum_{I=1}^P \frac{\hbar^2}{2M_I} \nabla_I^2}_{K_N} + \underbrace{\frac{e^2}{2} \sum_{I=1}^P \sum_{J \neq I}^P \frac{Z_I Z_J}{|R_I - R_J|}}_{V_{NN}} - \\
 & \underbrace{-\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2}_{K_e} + \underbrace{\frac{e^2}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|r_i - r_j|}}_{V_{ee}} - \\
 & \underbrace{-e^2 \sum_{I=1}^P \sum_{i=1}^N \frac{Z_I}{|R_I - r_i|}}_{V_{Ne}}
 \end{aligned}$$

Schrödinger equation

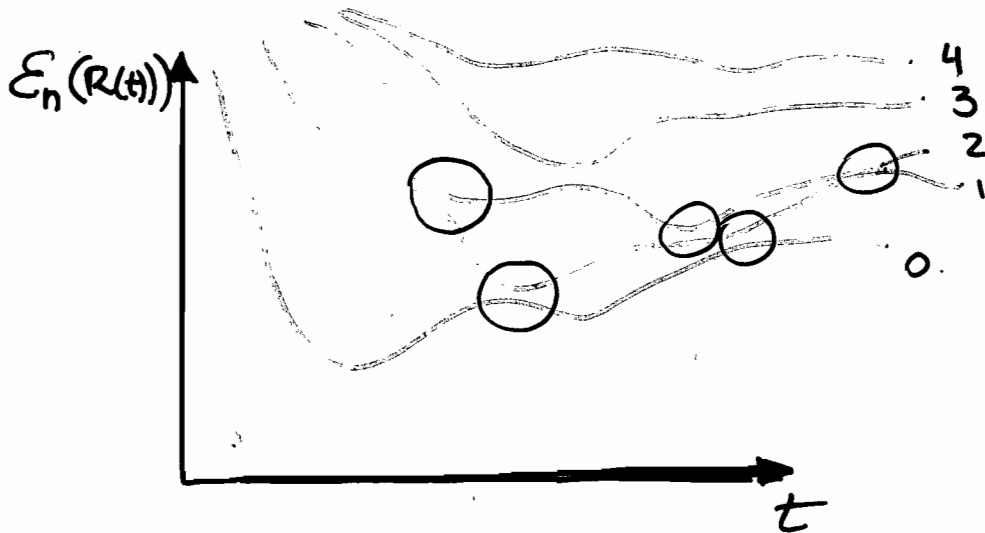
$$\begin{aligned}
 \hat{H} \psi_i(r, R) &= E_i \psi_i(r, R) \\
 [i\hbar \frac{\partial \psi_i}{\partial t} &= \hat{H} \psi]
 \end{aligned}$$

$$\begin{cases}
 r = \{r_i\} & i=1, \dots, N \\
 R = \{R_I\} & I=1, \dots, P \\
 3(P+N) & \text{degrees of freedom}
 \end{cases}$$

Adiabatic Approximation

$$m_p \sim 1836 m_e$$

"Electrons follow instantaneously the motion of the nuclei", without changing eigenstate of the electronic Hamiltonian.



$$\psi(r, R, t) = \sum_n \Theta_n(R, t) \phi_n(r, R)$$

Adiabatic expansion
(basis)

$$\hat{h}_e = \hat{K}_e + \hat{V}_{ee} + \hat{V}_{Ne}^{(R)} = \hat{H} - \hat{K}_N - \hat{V}_{NN}$$

electronic Hamiltonian.

$$\hat{h}_e(R) \phi_n(r, \underline{R}) = E_n(\underline{R}) \phi_n(r, \underline{R})$$

\underline{R} (nuclear configuration)

enters as a parameter.

In principle one should solve the above for all R and all involved n (states).

Replacing the expansion in the adiabatic basis into the time-dependent Schrödinger eq.:

$$\left\{ i\hbar \frac{\partial}{\partial t} + \sum_{I=1}^P \frac{\hbar^2}{2M_I} \nabla_I^2 - E_q(R) \right\} \Theta_q(R, t) =$$

$$= \sum_{I=1}^P \frac{\hbar^2}{2M_I} \langle \phi_q | \nabla_I^2 | \phi_q \rangle \Theta_q(R, t) +$$

$$+ 2 \sum_{m \neq q} \sum_{I=1}^P \frac{\hbar^2}{2M_I} \left[\nabla_I \Theta_m(R, t) \right] \cdot \underbrace{\langle \phi_q | \nabla_I | \phi_m \rangle}_{\substack{\text{dip.} = \text{Non-radiative} \\ \text{coupling.}}}$$

**NON-RADIATIVE ELECTRONIC TRANSITIONS
 EXCITED BY THE NUCLEAR MOTION**

Condition for adiabaticity

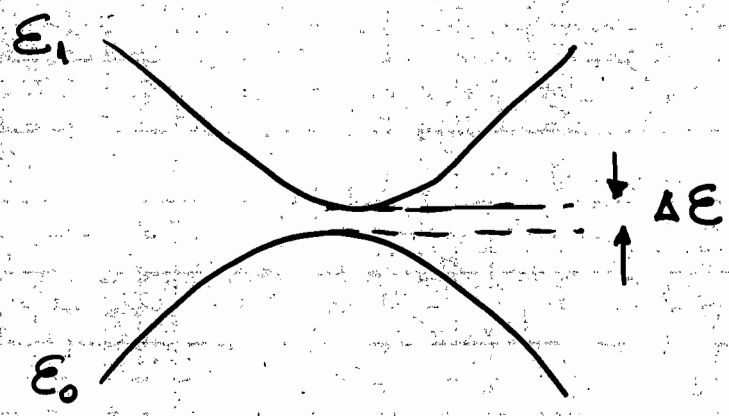
$$\left| \sum_{I=1}^P \frac{\hbar^2}{M_I} \langle \Theta_q | \nabla_I | \Theta_m \rangle \cdot \langle \phi_m | \nabla_I | \phi_q \rangle \right| \ll \left| \langle E_q(R) - E_m(R) \rangle \right|$$

$$\frac{m}{M_I} \left| \frac{\hbar \Omega_{\nu}}{E_q(R) - E_m(R)} \right| \ll 1$$

Ω_{ν} = frequency of rotation of the electronic wf. due to the nuclear motion.

$\frac{m}{M_I} \lesssim 5 \times 10^{-4}$; $\Delta E \sim 1 \text{ eV}$ } the above is normally verified.
 $\hbar \Omega_{\nu} \sim 0.01 \text{ eV}$

(L ANDAU - ZENER) AVOIDED CROSSINGS



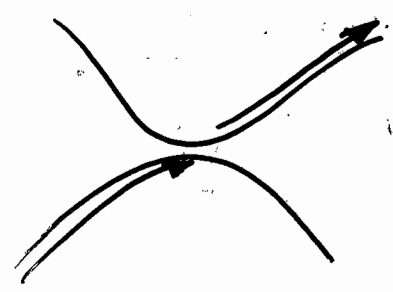
$$P_{\text{jump}} \propto e^{-\alpha \frac{\Delta E}{v}}$$

1) ΔE small or v large: P_{jump} large DIABATIC

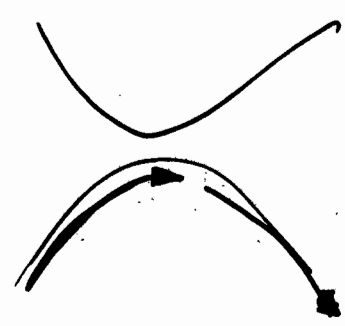
↓
Metallic systems

e^- -ph perturbative or Adiabatic

(Plasmon ~ 2 eV is more relevant than $e-h$ pairs).



2) ΔE large or v small: P_{jump} small ADIABATIC



Reality is a bit more complicated, but this is qualitatively correct. SYSTEM CAN STAY OR CHANGE LEADING TO MULTIPLE TRAJECTORIES



Adiabatic electronic eigenstates are not mixed.

$$\therefore \psi(r, R, t) \equiv \Theta_m(R, t) \Phi_m(R, r)$$

m doesn't change, e.g. $n=0$ (Ground state).

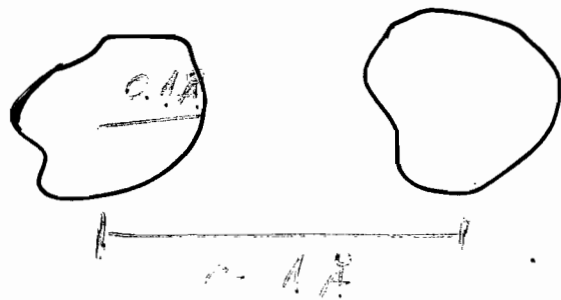
⇒ Adiabatic Schrödinger equation:

$$\left\{ i\hbar \frac{\partial}{\partial t} + \sum_{I=1}^P \frac{\hbar^2}{2M_I} \nabla_I^2 - \epsilon_m(R) - \underbrace{\sum_{I=1}^P \frac{\hbar^2}{2M_I} \langle \Phi_m | \nabla_I^2 | \Phi_m \rangle}_{\text{A phase-energy correction}} \right\} \Theta_m(R, t) = 0$$

CLASSICAL NUCLEI APPROXIMATION.

Thermal wavelength (room T) $\sim 0.1 \text{ \AA}$

⇒ No phase coherence



$$\Theta_m(R, t) \equiv \prod_I \underbrace{\Theta_m^{(I)}(R, R_c^{(I)}(t), t)}_{\text{Product of single-particle wfn. (Hartree approximation)}}$$

Product of single-particle wfn.

(Hartree approximation)

- Quantum \rightarrow classical transition (decoherence)

$$i\hbar \frac{\partial \Psi_m(\mathbf{R}, t)}{\partial t} = \left(- \sum_{\mathbf{I}=1}^P \frac{\hbar^2}{2M_{\mathbf{I}}} \nabla_{\mathbf{I}}^2 - E_n(\mathbf{R}) \right) \Psi_m(\mathbf{R}, t)$$

Wave-packets are quite localized, e.g. $\sim 0.25 \text{ \AA}$ for H in a typical bonding environment (this is almost the worst case). Typically the mass is larger and localization as well.

\therefore Classical nuclei approximation.

Ehrenfest's theorem:

$$i\hbar \frac{\partial \langle \mathbf{R}_{\mathbf{I}} \rangle}{\partial t} = \langle [\hat{H}, \hat{\mathbf{R}}_{\mathbf{I}}] \rangle = i\hbar \frac{\langle \mathbf{P}_{\mathbf{I}} \rangle}{M_{\mathbf{I}}} \Rightarrow M_{\mathbf{I}} \frac{d\langle \mathbf{R}_{\mathbf{I}} \rangle}{dt} = \langle \mathbf{P}_{\mathbf{I}} \rangle$$

$$i\hbar \frac{\partial \langle \mathbf{P}_{\mathbf{I}} \rangle}{\partial t} = \langle [\hat{H}, \hat{\mathbf{P}}_{\mathbf{I}}] \rangle = -i\hbar \langle \nabla_{\mathbf{I}} E_n(\mathbf{R}) \rangle$$

\Rightarrow Newton's equations:
-like

$$M_{\mathbf{I}} \frac{d^2 \langle \mathbf{R}_{\mathbf{I}} \rangle}{dt^2} = - \langle \nabla_{\mathbf{I}} E_n(\mathbf{R}) \rangle$$

Valid for mean values

1) Nuclear wfn. approximated as a product of δ -funct.

$$\Psi_m^{(\mathbf{I})}(\mathbf{R}_{\mathbf{I}}, \mathbf{R}_{\mathbf{I}}^c(t), t) \rightarrow \delta(\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{I}}^c(t)) \quad \text{or}$$

$$\langle \mathbf{R}_{\mathbf{I}} \rangle = \mathbf{R}_{\mathbf{I}}^c(t) \quad \delta(\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{I}}^c(t))$$

2) $\langle \nabla_{\mathbf{I}} E_n(\mathbf{R}) \rangle \approx \nabla_{\mathbf{I}} E_n(\mathbf{R}^c) = \frac{\partial E_n(\mathbf{R}^c)}{\partial \mathbf{R}_{\mathbf{I}}^c}$ VALID ONLY FOR δ -fct. or harmonic potentials.

ERROR \propto ANHARMONICITY.

Finally:

$$M_I \frac{d^2 R_I(t)}{dt^2} = - \nabla_I E_n(R_{el})$$

PES.

Hellmann-Feynman theorem:

$$E_n = \langle \phi_n | \hat{h}_e | \phi_n \rangle$$

$$\frac{\partial E_n(a)}{\partial a} = \langle \phi_n(R) | \frac{\partial \hat{h}_e(a)}{\partial a} | \phi_n(R) \rangle$$

$$\Rightarrow M_I \frac{d^2 R_I^{(m)}(t)}{dt^2} = - \langle \phi_n(R^{(m)}) | \frac{\partial \hat{h}_e(R^{(m)})}{\partial R_I^{(m)}} | \phi_n(R^{(m)}) \rangle - \frac{\partial V_{NN}(R^{(m)})}{\partial R_I^{(m)}}$$

FIRST-PRINCIPLES QUANTUM

MOLECULAR DYNAMICS.

$$\nabla E_n(R^{(m)}) = 0$$

GEOMETRY OPTIMIZATION.

$$\hat{h}_e \phi_n(r, R^{(m)}) = E_n(R^{(m)}) \phi_n(R^{(m)})$$

ELECTRONIC STRUCTURE

"Solve stationary Schrödinger eq. for a system of N interacting electrons in the external Coulomb field of the nuclei"

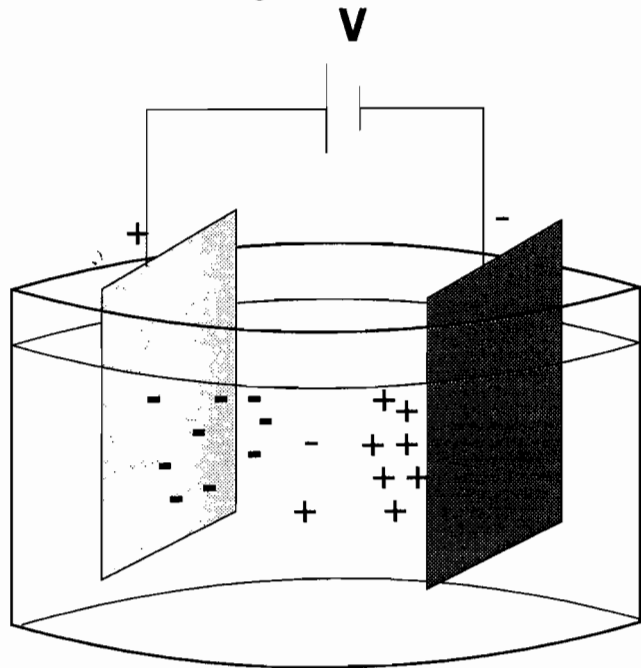
QUANTUM MANY-BODY PROBLEM

The Physical origin of many-body effects (correlation)

- Electrochemical cell

"Charge in the electrodes depends on the potential difference V ".

- screening length
- plasma frequency



Gouy -
CHAPMAN
1903-1913.

Many-body : electron in interaction with other electrons.

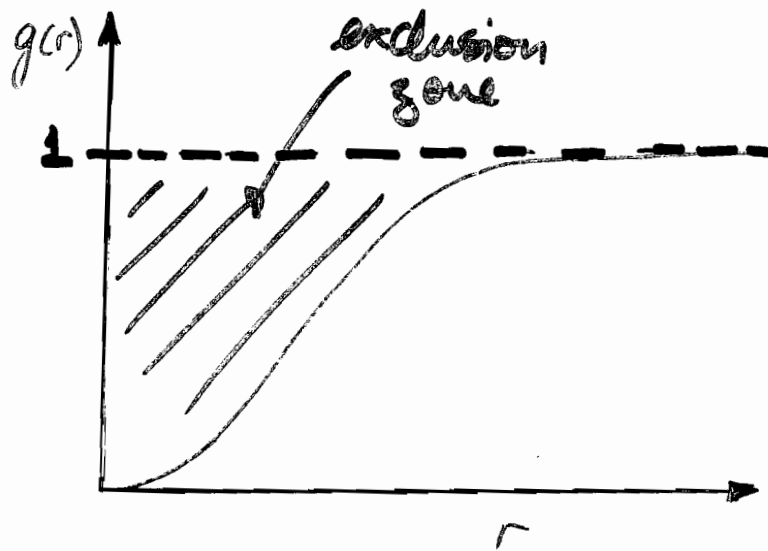
Electrostatics :
(Poisson)

$$\nabla^2 \psi_H(\mathbf{r}) = -4\pi \left\{ -e \delta(\mathbf{r}) - \underbrace{en(\mathbf{r})}_{\substack{\text{other} \\ e^-}} + e\bar{n} \right\}$$

\downarrow
 e^- at the origin

Define $g(\mathbf{r}) = \frac{n(\mathbf{r})}{\bar{n}}$ pair correlation function.

$$\nabla^2 V_H(r) = -4\pi e^2 \{ \delta(r) + \bar{n} [g(r) - 1] \}$$



"The presence of one electron at the origin ~~discourages~~ **discourages** the other electrons to come close to the origin".

$g(r)$ is the probability of finding ~~an~~ two electrons at a distance r .

CORRELATION!

Not just Quantum:

Boltzmann: $g(r) = e^{-V_H(r)/k_B T}$ classical particles.

linearization $g(r) \sim 1 - V_H(r)/k_B T$

+ Poisson $\Rightarrow \nabla^2 V_H(r) = -4\pi e^2 \delta(r) + \frac{1}{\epsilon_0} \frac{dV_H}{dr}$

$$V_H(r) = \frac{e^2}{r} e^{-r/\lambda_{DH}}$$

Screened Coulomb

$$\lambda_{DH} = \sqrt{\frac{k_B T}{4\pi n e^2}}$$

DEBYE HÜCKEL Screening length

QUANTUM



$q = \text{test charge}^{10}$

Electric field interacts with test charge:

$$E_q^{(r)} = q \left\{ \sum_I \frac{Z_I e}{|R_I - r|} + \int \frac{(-e) \rho(r')}{|r' - r|} dr' \right\}$$

$q \rightarrow -e$ (one electron amongst the others)
NOT A TEST CHARGE ANYMORE

$$V_{ee}^{(r)} = - \sum_I \frac{Z_I e^2}{|R_I - r|} + e^2 \int \frac{[\rho(r') + \delta\rho(r')]}{|r' - r|} dr'$$

$\delta\rho(r) = \text{static screening charge}$ [displaces charge to make space for itself.]
 \Downarrow Schrödinger eq.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{en}(r, R) + \underbrace{e^2 \int \frac{\rho(r')}{|r - r'|} dr'}_{\text{ELECTR.}} + \underbrace{V_{\text{screen}}(r)}_{\text{correlation}} \right] \psi_{\mu}(r) = E_{\mu} \psi_{\mu}(r)$$

- 1) Fermi-Dirac statistics \Rightarrow Exchange (a form of correlation)
- 2) Non-statistical correlations (static and dynamical)
- 3) Pauli principle $\Rightarrow \rho(r) = \sum_{\nu=1}^N |\psi_{\nu}(r)|^2$

HOMOGENEOUS ELECTRON GAS (JELIUM)

$$V_{\text{screen}}(\underline{r}) = e^2 \int \frac{\rho(\underline{r}') d\underline{r}'}{|\underline{r}-\underline{r}'|}$$

$$V_H(\underline{r}) = e^2 \int \frac{\rho(\underline{r}') d\underline{r}'}{|\underline{r}-\underline{r}'|} \quad (1) \quad \text{Poisson.}$$

Random Phase Approximation (RPA):

$$\rho(\underline{r}) = -\frac{m k_F^2}{2\pi^3 \hbar^2} \int V_H(\underline{r}') \frac{j_1(2k_F |\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|^2} d\underline{r}' \quad (2)$$

Dielectric function : $V_H(\underline{k}) = \frac{4\pi e^2}{k^2 \epsilon(\underline{k})}$ (Rec. space)

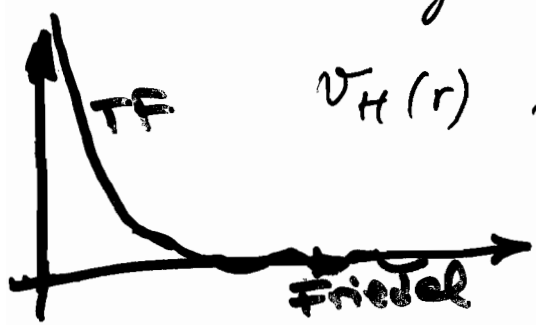
(1) + (2) $\Rightarrow V_H(\underline{r}) \Rightarrow \epsilon(\underline{k})$

$$\epsilon_{\text{RPA}}(\underline{k}) = 1 + \frac{2m k_F e^2}{5\pi \hbar^2 k^2} \left\{ 1 + \frac{k_F}{k} \left(\frac{k^2}{4k_F^2} - 1 \right) \ln \left| \frac{k-2k_F}{k+2k_F} \right| \right\}$$

LINDHARD FUNCTION

Small k : $V_H(\underline{k}) \sim \frac{4\pi e^2}{k^2 + (k_{TF})^2} \rightarrow \boxed{V_{\text{screen}}(\underline{r}) = \frac{e^2}{r} e^{-k_{TF} r}}$
Thomas-Fermi screening length

k \rightarrow 2k_F : log. singularity



$V_H(r) \sim -2 A e^2 \frac{\cos(2k_F r)}{r^3}$ large r

Friedel oscillations

Quantum-Chemical approaches

-13-

Hartree: $\Phi(r, R) = \prod_i \varphi_i(r_i, R)$
 (Mean-Field)

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}^{(i)}(r_i, R) \right] \varphi_i(r_i, R) = \epsilon_i \varphi_i(r_i, R)$$

$$V_{\text{eff}}^{(i)}(r_i, R) = V_{\text{ext}}(r_i, R) + \int \frac{\sum_{j \neq i}^N \rho_j(r_j')}{|r_i - r_j'|} dr_j'$$

$$\rho_j(r) = |\varphi_j(r, R)|^2$$

Notice self-interaction removal!

$$E_H = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} dr dr'$$

Double-counting.

Hartree-Fock: $\Phi(r, R) = \text{SD} \{ \varphi_j(r_i, R) \}$
 Slater determinant.

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(r_i, R) + \int \frac{\sum_{j=1}^N \rho_j(r_j')}{|r_i - r_j'|} dr_j' \right] \varphi_i(r_i, R) =$$

$$- \sum_{j=1}^N \left(\int \frac{\varphi_j^*(r_j') \varphi_i(r_j')}{|r_i - r_j'|} dr_j' \right) \varphi_j(r_i, R) = \sum_{j=1}^N A_{ij} \varphi_j(r_i, R).$$

EXCHANGE.

- Perturbation Theory (MP2 - MP4)
- Configuration Interaction (CI / CAS)

Why beyond HF?

Energy of an inhomogeneous electron system:

$$E = \langle \phi | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} | \phi \rangle \quad \text{Ground state expectation value}$$

$|\phi\rangle = N$ -electron wave function.

- 0 - (Hartree) : $|\phi\rangle = \varphi_1(r_1) \cdot \varphi_2(r_2) \dots \varphi_N(r_N)$

- 1 - (Hartree-Fock) : $|\phi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \varphi_1(r_2) & \dots & \varphi_1(r_N) \\ \varphi_2(r_1) & \varphi_2(r_2) & \dots & \dots \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(r_1) & \varphi_N(r_2) & \dots & \varphi_N(r_N) \end{vmatrix}$

- 2 - (CI) $|\phi\rangle = \sum_{i_1, \dots, i_N} c_{i_1, \dots, i_N}^{SD} \{ \varphi_{i_1}(r_1) \dots \varphi_{i_N}(r_N) \}$
 $\{i_1, \dots, i_N\}$: configuration.

HF takes care ONLY of exchange.

CI includes correlation. (CISD)

ELECTRON-ELECTRON INTERACTION (GENERAL)

$$E_{\text{ee}} = \langle \phi | \hat{V}_{\text{ee}} | \phi \rangle = \langle \phi | \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\underline{r}_i - \underline{r}_j|} | \phi \rangle =$$

$$= \iint \frac{\rho_2(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}'$$

$$\rho_2(\underline{r}, \underline{r}') = \text{TWO-BODY DENSITY MATRIX.}$$

$$= \frac{1}{2} \langle \phi | \hat{\psi}^\dagger(\underline{r}) \hat{\psi}^\dagger(\underline{r}') \hat{\psi}(\underline{r}') \hat{\psi}(\underline{r}) | \phi \rangle$$

$\hat{\psi}(\underline{r})$ annihilates an electron at \underline{r}

$\hat{\psi}^+(\underline{r})$ creates an electron at \underline{r}

$$\{ \hat{\psi}(\underline{r}), \hat{\psi}^+(\underline{r}') \} = \delta(\underline{r} - \underline{r}') \quad \text{ANTICOMMUTATION RELATION.}$$

Define the TWO-BODY DIRECT CORRELATION FUNCTION AS:

$$\rho_2(\underline{r}, \underline{r}') = \frac{1}{2} \rho_1(\underline{r}, \underline{r}) \rho_1(\underline{r}', \underline{r}') g(\underline{r}, \underline{r}')$$

(Diagonal)
 ONE-BODY DENSITY MATRIX

$$\rho_1(\underline{r}, \underline{r}') = \langle \phi | \hat{\psi}^+(\underline{r}) \hat{\psi}(\underline{r}') | \phi \rangle$$

$$\rho_1(\underline{r}, \underline{r}) = \rho(\underline{r}) = \text{ELECTRONIC DENSITY}$$

THEREFORE:

$$E_{ee} = \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} [g(\underline{r}, \underline{r}') - 1] d\underline{r} d\underline{r}'$$

DIRECT (HARTREE)
 COULOMB
 (Classical electrostatics)

PAIR
 CORRELATION
 FUNCTION.

(includes exchange)

in Hartree-Fock:

CORRELATION HOLE MISSING.

$$g(\underline{r}, \underline{r}') = 1 - \frac{1}{2} \frac{\rho_1(\underline{r}, \underline{r}')}{\rho(\underline{r}) \rho(\underline{r}')}$$

EXCHANGE HOLE.
 $g = g_x$

Total energy (GENERAL):

E_{ee}

$$E = T + V_{\text{ext}} + \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + E_x + E_c$$

\downarrow \downarrow \downarrow \downarrow \downarrow
 Kinetic external Hartree Exchange Correl. (Direct Coulomb)

$$V_{\text{ext}} = \sum_{i=1}^P \int \rho(\underline{r}) V_{\text{ext}}(\underline{r} - \underline{R}_i) d\underline{r}$$

$$T = -\frac{\hbar^2}{2m} \langle \phi | \sum_{i=1}^N \nabla_i^2 | \phi \rangle = -\frac{\hbar^2}{2m} \int [\nabla_r^2 \rho(\underline{r}, \underline{r}')] \Big|_{\underline{r}' = \underline{r}} d\underline{r}$$

DFT

THOMAS - FERMI (1927)

Approximation for the Kinetic energy.

Uniform electron gas: $\left\{ \begin{array}{l} \rho = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2} \\ T = \frac{3}{5} \rho E_F \end{array} \right.$

$$\hookrightarrow t[\rho] = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \rho^{5/3}$$

Kinetic energy density from the UEG.

$$E_{TF} = C_k \int \rho(\underline{r})^{5/3} d\underline{r} + \int V_{\text{ext}}(\underline{r}) \rho(\underline{r}) d\underline{r} + \frac{1}{2} \iint \frac{\rho(\underline{r}) \rho(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}'$$

DEPENDS ONLY ON ρ .

Minimizing the energy with respect to $\rho(\mathbf{r})$
 [functional minimization \Rightarrow Functional derivative].

Constraint: $\int \rho(\mathbf{r}) d\mathbf{r} = N$ (Number of electrons)

Dispersion: $\frac{\delta F[g]}{\delta g} = \lim_{\Delta g \rightarrow 0} \frac{F[g+\Delta g] - F[g]}{\Delta g}$

with $g = g(\mathbf{r})$.

e.g. $F[g] = \int f[g(\mathbf{r})] d\mathbf{r}$

$$\frac{\delta F[g]}{\delta g(\mathbf{r})} = \left. \frac{df[g]}{dg} \right|_{g(\mathbf{r})}$$

for Thomas-Fermi:

$$\frac{5}{3} C_x \rho^{2/3}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \mu$$

$$\left(\frac{\delta E_{\text{TF}}[\rho]}{\delta \rho(\mathbf{r})} - \mu \frac{\delta}{\delta \rho(\mathbf{r})} \int \rho(\mathbf{r}) d\mathbf{r} = 0 \right)$$

\rightarrow Lagrange
 Multiplier
 arising from
 the charge
 normalization
 constraint
 (chem. pot.)

This connects univocally ρ and V_{ext} .
 Inversion $\Rightarrow \rho(\mathbf{r})$.

- Improvements:
- 1) Exchange: $E_x[\rho] = -C_x \rho^{4/3}(\mathbf{r})$ TF Dirac
 - 2) Correlation: $E_c[\rho] = -A \rho^{4/3} / (B + \rho^{1/3})$ Wigner
 - 3) Kinetic: $T_{\text{ov}}[\rho] = \frac{1}{8} \int \frac{|\nabla \rho|^2}{\rho} d\mathbf{r}$ von Weizsäcker

BEYOND ...
 Lin. Response
 (E. Carter)

MODERN DFT

Hohenberg-Kohn theorem (1964)

Two external local potential differing only in an additive constant, correspond to the same electronic density.

$$\rho(\mathbf{r}) \Leftrightarrow v(\mathbf{r}), \quad \underline{N}$$

number of electrons.

v-representability: Not any $\rho(\mathbf{r})$ is allowed. It must arise from some external potential $v(\mathbf{r}) \rightarrow$ Constrained search (M. Levy - 1982).

Minimum principle $= \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$

$$E_v[\rho] = T[\rho] + V_{\text{ext}}[\rho] + E_{\text{ee}}[\rho]$$

is minimum for $\bar{\rho} =$ GROUND STATE DENSITY.

Variational equations

$$\delta [E_v[\rho] - \mu (\int \rho(\mathbf{r}) d\mathbf{r} - N)] = 0$$

$$\delta E_v[\rho] / \delta \rho = v_{\text{ext}}(\mathbf{r}) + \delta F[\rho] / \delta \rho = \mu.$$

$$F[\rho] = T[\rho] + E_{\text{ee}}[\rho]$$

UNIVERSAL FUNCTIONAL.

(DEPENDS ONLY ON THE INTERACTION)

DENSITY FUNCTIONAL THEORY

-20-

Hohenberg-Kohn theorem.

1) $\rho(\mathbf{r}) \longleftrightarrow V(\mathbf{r})$

2) $E_0 = E[\rho_{GS}(\mathbf{r})] = \int \rho_{GS}(\mathbf{r}) \overbrace{V(\mathbf{r})}^{V_{ext}} + F[\rho_{GS}]$

where: $F[\rho] = \min_{\{\psi\} \rightarrow \rho} \langle \psi | \hat{T} + \hat{U} | \psi \rangle$ (constrained search)

is a UNIVERSAL functional which depends ONLY on the form of the electron-electron interaction \hat{U} .

HK theorem is valid for ANY \hat{U} , including $\hat{U} = 0$ (non-interacting electrons).

Define NON-INTERACTING REFERENCE SYSTEM

(R) as a system for which $\hat{U}_R = 0$, but the density is the same as in the interacting system with $\hat{U} \neq 0$.

$$\hat{H}_R = \hat{T}_R + \hat{V}_R \quad (\hat{V}_R \neq \hat{V}_{ext})$$

local potential

Single-particle ^{reference} orbitals $\varphi_j^R(\mathbf{r})$, such that

$\rho_R(\mathbf{r}) = \sum_{j=1}^N |\varphi_j^R(\mathbf{r})|^2 = \rho(\mathbf{r})$ [same density]

verify:

Key assumption.

SINCE REFERENCE ELECTRONS DON'T INTERACT DIRECTLY, THEY VERIFY THE STANDARD SCHRÖDINGER EQUATION IN THE "EXTERNAL" POTENTIAL $V_R[\rho](\underline{r})$:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_R[\rho](\underline{r}) \right] \varphi_j^R(\underline{r}) = \epsilon_j \varphi_j^R(\underline{r})$$

$\varphi_j^R(\underline{r})$ ARE IMPLICITLY FUNCTIONALS OF ρ .

THE ENERGY OF NON-INTERACTING ELECTRONS IS:

$$E_R[\rho] = T_R[\rho] + \int \rho(\underline{r}) V_R(\underline{r}) d\underline{r}$$

WITH:

$$T_R[\rho] = \sum_{i=1}^{N_{occ}} \int \varphi_i^R(\underline{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_i^R(\underline{r}) d\underline{r}$$

\therefore ALSO T_R IS AN IMPLICIT FUNCTIONAL OF ρ VIA:

$$\rho(\underline{r}) \rightarrow V_R[\rho] \rightarrow \{ \varphi_i^R(\underline{r}) \} \rightarrow T_R[\rho]$$

ANY FUNCTIONAL OF THE REFERENCE ORBITALS IS, IMPLICITLY, A FUNCTIONAL OF ρ .

Define, for the INTERACTING system,
the Exchange-Correlation functional as:

$$E_{xc}[\rho] = F[\rho] - \underbrace{\frac{1}{2} \iint \frac{\rho(\underline{r})\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}d\underline{r}'}_{\text{DIRECT COULOMB}} - \underbrace{T_R[\rho]}_{\substack{\text{K.E. of} \\ \text{the Non-interacting} \\ \text{reference system} \\ \text{(same } \rho \text{!!)}}}$$

• $E_{xc}[\rho]$ is different from

$$E_{xc}^{int}[\rho] = F[\rho] - \frac{1}{2} \iint \frac{\rho(\underline{r})\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}d\underline{r}' - \underbrace{T[\rho]}_{\substack{\text{K.E. of the} \\ \text{INTERACTING system}}}$$

($T[\rho] \neq T_R[\rho]$).

therefore, the HK energy is:

$$E_H[\rho] = T_R[\rho] + \int \rho(\underline{r}) v_{ext}(\underline{r}) d\underline{r} + \frac{1}{2} \iint \frac{\rho(\underline{r})\rho(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}d\underline{r}' + E_{xc}[\rho]$$

↳ only unknown term.

Thomas-Fermi-like methods: Approx. $T_R[\rho]$ explicitly \Rightarrow VERY FAST.
NO GOOD APPROX. FOR $T_R[\rho]$.

KOHN-SHAM METHODS

W. KOHN AND L. SHAM, 1965.

+ EXACT $T_R[\rho]$ via reference orbitals φ_i^R
 - APPROXIMATE $E_{xc}[\rho]$

$E_J[\rho]$ is VARIATIONAL \Rightarrow MINIMIZE E w.r.t. ρ

$$0 = \frac{\delta E_J}{\delta \rho(\mathbf{r})} = \frac{\delta T_R[\rho]}{\delta \rho(\mathbf{r})} + \underbrace{V_{\text{ext}}(\mathbf{r}) + V_H[\rho](\mathbf{r}) + \mu_{xc}[\rho](\mathbf{r})}_{V_{KS}[\rho](\mathbf{r})}$$

$V_{KS}[\rho](\mathbf{r})$ KOHN-SHAM
POTENTIAL.

$$\mu_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad \text{EXCHANGE-CORREL. POTENTIAL.}$$

Remember $T_R[\rho] = T_R[\{\varphi_i^R[\rho]\}]$.

$$\Rightarrow \delta T_R[\rho] = \delta \left(\sum_{i=1}^{N_{\text{occ}}} \int \underline{\varphi_i^R(\mathbf{r})} \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \underline{\varphi_i^R(\mathbf{r})} d\mathbf{r} \right)$$

$$\text{USING } -\frac{\hbar^2}{2m} \nabla^2 \varphi_i^R(\mathbf{r}) = \epsilon_i \varphi_i^R(\mathbf{r}) - V_R(\mathbf{r}) \varphi_i^R(\mathbf{r})$$

AND FIRST-ORDER PERT. THEORY FOR $\delta \epsilon_i$:

$$\delta T_R[\rho] = - \int V_R[\rho](\mathbf{r}') \delta \rho(\mathbf{r}') d\mathbf{r}'$$

$$\therefore \boxed{\frac{\delta T_R[\rho]}{\delta \rho(\mathbf{r})} = -V_R[\rho](\mathbf{r})} \quad \text{ALWAYS VALID.}$$

THEREFORE, THE REFERENCE POTENTIAL $V_R[\rho]$ COINCIDES WITH THE KOHN-SHAM POTENTIAL:

$$V_R[\rho] = V_{KS}[\rho] = V_{ext}(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r})$$

KOHN-SHAM EQUATIONS:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[\rho](\mathbf{r}) \right\} \psi_i^{KS}(\mathbf{r}) = \epsilon_i \psi_i^{KS}(\mathbf{r})$$

WHERE:

$$\rho(\mathbf{r}) = \rho^{KS}(\mathbf{r}) = \sum_{i=1}^{N_{occ}} |\psi_i^{KS}(\mathbf{r})|^2$$

INTERACTING AND REFERENCE DENSITIES ARE EQUAL (v -representability)

- $\Psi_{\text{int}}(\underline{r}_1 \dots \underline{r}_N) \neq \text{SD} \{ \varphi_1(\underline{r}_1) \dots \varphi_N(\underline{r}_N) \}$

but:
$$\rho(\underline{r}) = N \int \dots \int d\underline{r}_2 \dots d\underline{r}_N |\Psi_{\text{int}}(\underline{r}, \underline{r}_2, \dots, \underline{r}_N)|^2 =$$

$$= \sum_{i=1}^{N_{\text{occ}}} |\varphi_i(\underline{r})|^2$$

- $E_{\text{xc}}[\rho]$ contains also the kinetic correlations, which are not contained in $T_{\text{R}}[\rho]$. (~~more later~~)

- The NON-INTERACTING REFERENCE SYSTEM does not necessarily exist! (V-Representability).

Solution: Constrained search again! Extend the domain of definition of occupation numbers $\{f_i\}$, which were 0 or 1, to any real number between 0 and 1, and minimize w.r.t. f_i -

$$\rho(\underline{r}) = \sum_{i=1}^N f_i |\varphi_i(\underline{r})|^2 \quad N > N_{\text{occ}}.$$

- Janak's theorem is valid: $I = -\mu = -\epsilon_{\text{max}}$
 $[\epsilon_i = \partial E / \partial f_i]$

- Koopman's theorem is NOT valid

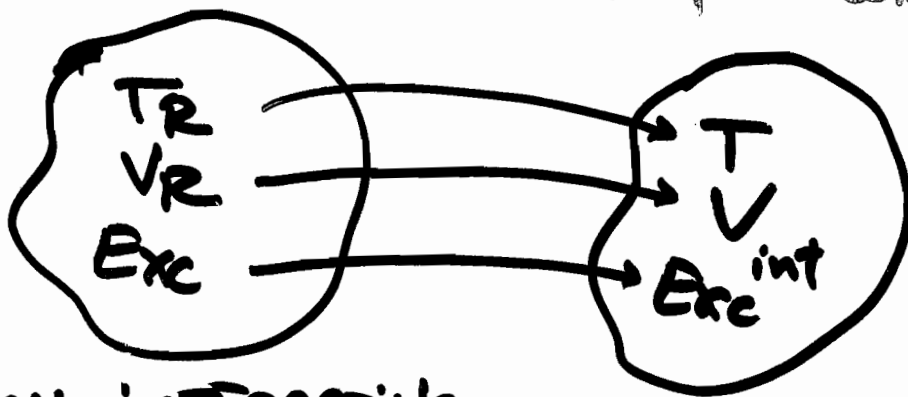
$$E(N+1) - E(N) \neq E_{\text{excitation}}.$$

(SLATER'S
 Δ SCF)

EXCHANGE-CORRELATION

$$E_{ee}[\rho] = E_H[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [g(\mathbf{r},\mathbf{r}') - 1] d\mathbf{r}d\mathbf{r}'$$

DIRECT COULOMB
 $E_{xc}^{int}[\rho]$
EXCHANGE & CORRELATION



NON-INTERACTING

KNOWING E_{xc}^{int} , HOW TO OBTAIN $E_{xc}[\rho]$ THAT ENTERS KOHN-SHAM EQUATIONS?

- START FROM NON-INT. AND SWITCH GRADUALLY THE COULOMB INTERACTION.

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{ext} + \lambda \hat{U}_{ee} \quad \lambda: 0 \rightarrow 1.$$

ALWAYS KEEPING THE SAME $\rho_\lambda(\mathbf{r}) = \rho(\mathbf{r}) \forall \lambda$. (ADIABATIC CONNECTION).

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [\tilde{g}(\mathbf{r},\mathbf{r}') - 1] d\mathbf{r}d\mathbf{r}'$$

WITH $\tilde{g}(\mathbf{r},\mathbf{r}') = \int_0^1 d\lambda g_\lambda(\mathbf{r},\mathbf{r}')$

LANGREITH
FERRELL 72

IN PRACTISE, E_{xc} IS OBTAINED AS THE DIFFERENCE $E_{xc} = E_{xc}^{int} + T[\rho] - T_R[\rho]$

TAKEN FROM EXACT CALCULATIONS (QMC.)

EXCHANGE: NO A-AVERAGE. CORRELATION DUE TO EXCHANGE ALREADY TAKEN INTO ACCOUNT VIA ORTHOGONALITY AND OCCUPATIONS (PAULI)

$$\tilde{g}(\zeta, \zeta') = g_x(\zeta, \zeta') + \tilde{g}_c(\zeta, \zeta')$$

WITH $g_x(\zeta, \zeta') = 1 - \frac{1}{2} \frac{\rho(\zeta, \zeta')}{\rho(\zeta)\rho(\zeta')}$

EXCHANGE-CORRELATION HOLE

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{\rho(\zeta)\tilde{\rho}_{xc}(\zeta, \zeta')}{|\zeta - \zeta'|} d\zeta d\zeta'$$

$$\tilde{\rho}_{xc}(\zeta, \zeta') = \underbrace{\rho(\zeta') [g_x(\zeta, \zeta')]}_{\tilde{\rho}_x(\zeta, \zeta')} + \underbrace{[\tilde{g}_c(\zeta, \zeta') - 1] \rho(\zeta')}_{\tilde{\rho}_c(\zeta, \zeta')}$$

PROPERTIES:

- SUM RULES { X-HOLE INTEGRATES TO -1
C-HOLE INTEGRATES TO 0

- SYMMETRY : $\tilde{\rho}(\zeta, \zeta') = \tilde{\rho}(\zeta', \zeta)$

- NORMALIZATION

SELF-INTERACTION

pair correlation function
 (la corrélation des paires électron-électron): $g_{ee}(r)$

-29-

(Perdeur & Wang, Phys. Rev. B 45, 12947 (1992)).

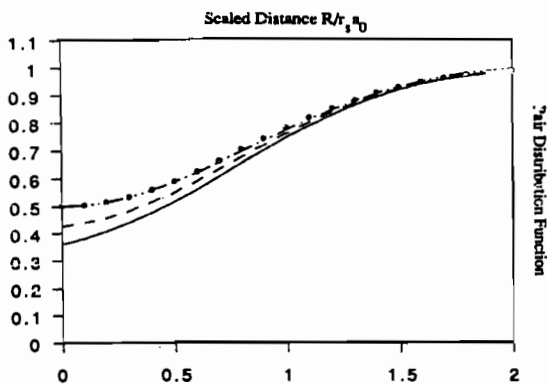


FIG. 1. Nonoscillatory part of the pair-distribution function $\langle g \rangle$ (solid curve) and its coupling constant average $\langle \bar{g} \rangle$ (dashed curve), for a uniform electron gas with density parameter $r_s = 0.5$ and spin polarization $\zeta = 0$. The high-density limit of $\langle g \rangle$ or $\langle \bar{g} \rangle$ is the exchange-only pair-distribution function $\langle g_x \rangle \approx g_x$ (dots).

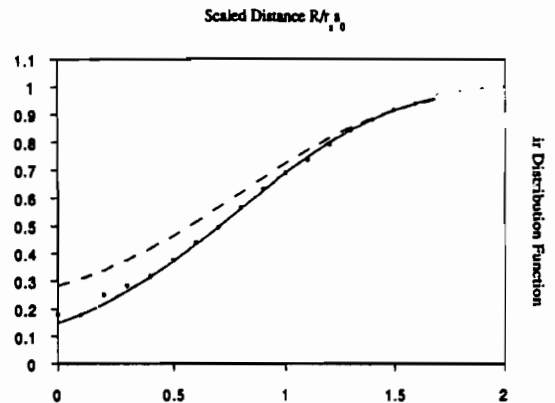


FIG. 3. Nonoscillatory part of the pair-distribution function $\langle g \rangle$ (solid curve) and its coupling-constant average $\langle \bar{g} \rangle$ (dashed curve), for a uniform electron gas with density parameter r_s and spin polarization ζ , compared with the result (heavy dots) of a quantum Monte Carlo calculation of g (Ref. 4). $r_s = 2$, $\zeta = 0$.

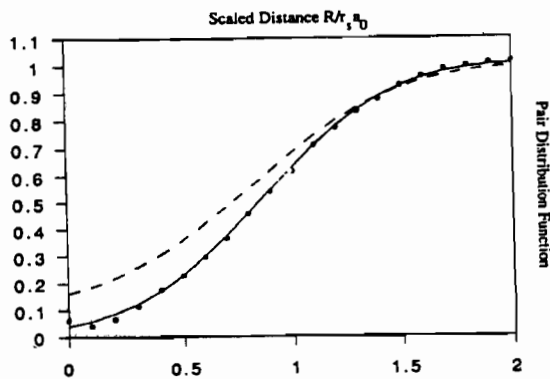


FIG. 4. Same as Fig. 3. $r_s = 5$, $\zeta = 0$.

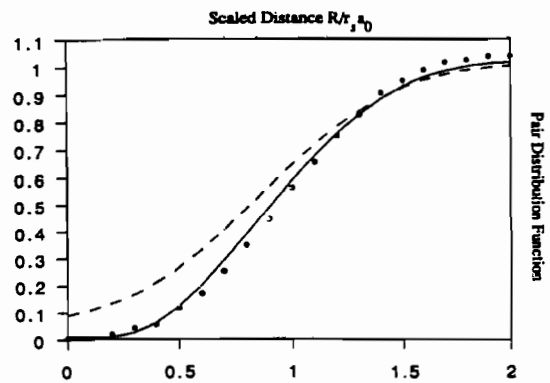


FIG. 5. Same as Fig. 3. $r_s = 10$, $\zeta = 0$.