Do we need the wave-function?

observable for N indistinguishable particles

$$M(\mathbf{x}) = M_0 + \sum_i M_1(x_i) + \frac{1}{2!}\sum_{i\neq j} M_2(x_i, x_j) + \frac{1}{3!}\sum_{i\neq j\neq k} M_3(x_i, x_j, x_k) + \cdots$$

$$= M_0 + \sum_i M_1(x_i) + \sum_{i<j} M_2(x_i, x_j) + \sum_{i<j<k} M_3(x_i, x_j, x_k) + \cdots$$

operators must be symmetric in particle coordinates,
if not they could be used to distinguish particles...

we use the wave-function as a **tool** for calculating observables

expectation values

expectation value

$$\langle M_1 \rangle = \int dx_1 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \sum_i M_1(x_i) \, \psi(x_1, \ldots, x_N)$$

$$= N \int dx_1 \, M_1(x_1) \underbrace{\int dx_2 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \, \psi(x_1, \ldots, x_N)}_{= \Gamma^{(1)}(x_1)}$$

for non-local operators, e.g. $M(x) = -\frac{1}{2} \Delta$

$$\langle M_1 \rangle = \int dx_1 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \sum_i M_1(x_i) \, \psi(x_1, \ldots, x_N)$$

$$= N \int dx_1 \lim_{x_1' \to x_1} M_1(x_1) \underbrace{\int dx_2 \cdots dx_N \, \overline{\psi(x_1', \ldots, x_N)} \, \psi(x_1, \ldots, x_N)}_{= \Gamma^{(1)}(x_1'; x_1)}$$

reduced density matrices

p-body density matrix of *N*-electron state
for evaluation of expectation values of M_p

$$\Gamma^{(p)}(x'_1,\ldots,x'_p;x_1,\ldots,x_p) =$$

$$\binom{N}{p}\int dx_{p+1}\cdots dx_N\,\overline{\Psi(x'_1,\ldots,x'_p,x_{p+1},\ldots,x_N)}\,\Psi(x_1,\ldots,x_p,x_{p+1},\ldots,x_N)$$

Hermitean ($x'\leftrightarrow x$) and antisymmetric under permutations of the x_i (or x_i')

normalization sum-rule $\int dx_1\cdots dx_p\,\Gamma^{(p)}(x_1,\ldots,x_p;x_1,\ldots,x_p) = \binom{N}{p}$

allows evaluation of expectation values of observables M_q with $q \le p$:
recursion relation

$$\Gamma^{(p)}(x'_1,\ldots,x'_p;x_1,\ldots,x_p) = \frac{p+1}{N-p}\int dx_{p+1}\Gamma^{(p+1)}(x'_1,\ldots,x'_p,x_{p+1};x_1,\ldots,x_p,x_{p+1})$$

Coulson's challenge

external potential $$\langle V \rangle = \left\langle \psi \left| \sum_i V(r_i) \right| \psi \right\rangle = \int dx\, V(r)\, \Gamma^{(1)}(x;x)$$

kinetic energy $$\langle T \rangle = \left\langle \psi \left| -\frac{1}{2} \sum_i \Delta_{r_i} \right| \psi \right\rangle = -\frac{1}{2} \int dx\, \Delta_r\, \Gamma^{(1)}(x';x) \Big|_{x'=x}$$

Coulomb repulsion $$\langle U \rangle = \left\langle \psi \left| \sum_{i<j} \frac{1}{|r_i - r_j|} \right| \psi \right\rangle = \int dx\, dx'\, \frac{\Gamma^{(2)}(x,x';x,x')}{|r-r'|}$$

minimize $E_{tot} = \langle T \rangle + \langle V \rangle + \langle U \rangle$ as a function of the
2-body density matrix $\Gamma^{(2)}(x_1',x_2';\, x_1,x_2)$
instead of the N-electron wave-function $\Psi(x_1,\ldots,\, x_N)$

representability problem:

what function $\Gamma(x_1',x_2';\, x_1,x_2)$ is a fermionic 2-body density-matrix?

exchange-correlation hole

electron density: $\Gamma(x; x) = n(x)$

conditional electron density: $2\Gamma(x, x'; x, x') = n(x, x')$

electron density at *x'* given that an electron is at *x*

Coulomb repulsion $\langle U \rangle = \int dx\, dx'\, \frac{\Gamma^{(2)}(x, x'; x, x')}{|r - r'|} = \frac{1}{2} \int dx\, dx' \frac{n(x, x')}{|r - r'|}$

rewrite in terms of Hartree energy

(how $\langle U \rangle$ differs from mean-field)

$$n(x, x') = n(x)n(x')\, g(x, x') = n(x)n(x') + n(x)n(x')\, (g(x, x') - 1)$$

pair correlation function

Hartree term

exchange-correlation hole

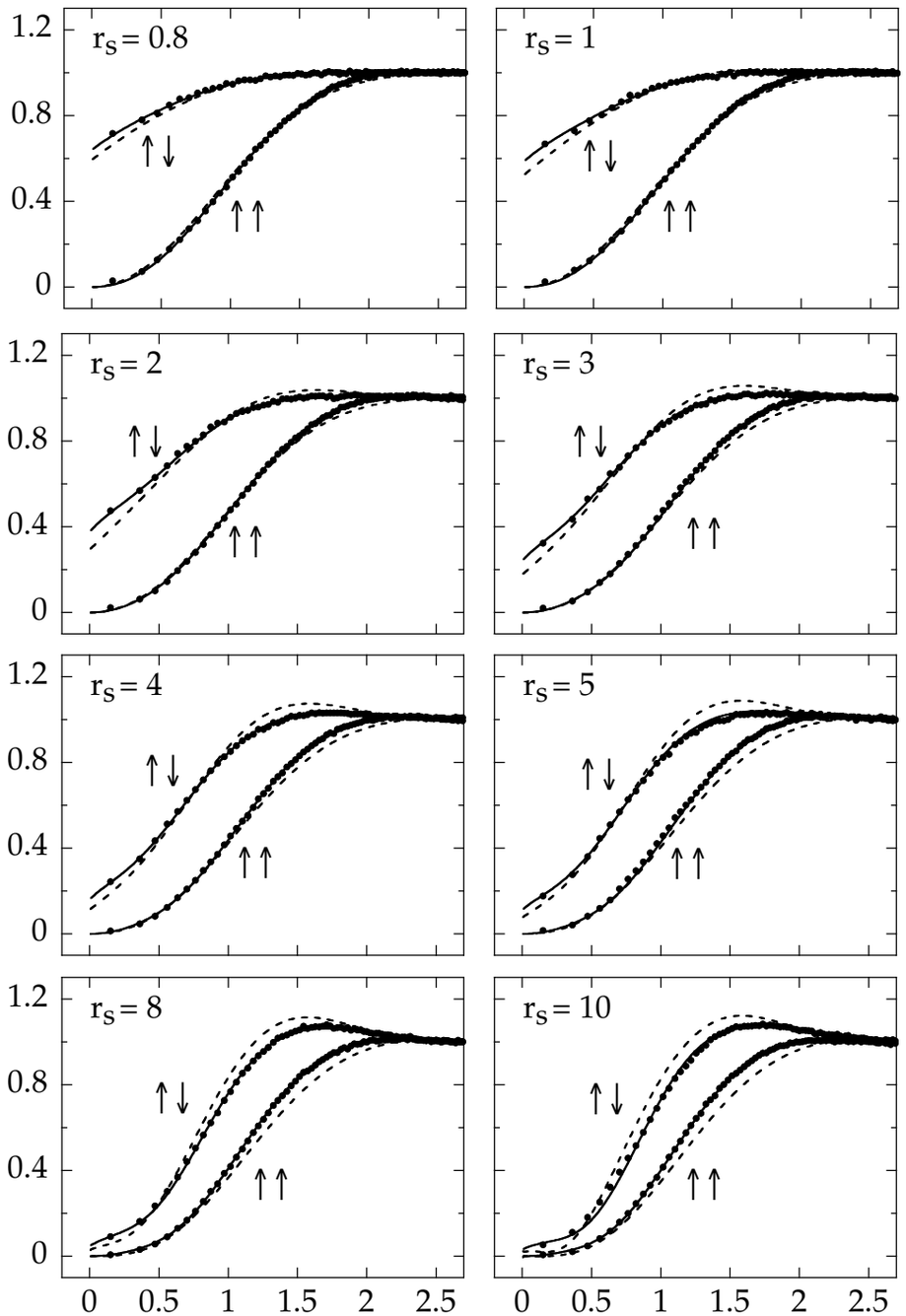
sum rule

$$\int dx'\, n(x, x') = n(x)\, (N - 1)$$

$$\int dx'\, n(x')\, \big(g(x, x') - 1\big) = -1$$

exchange-correlation holes from QMC

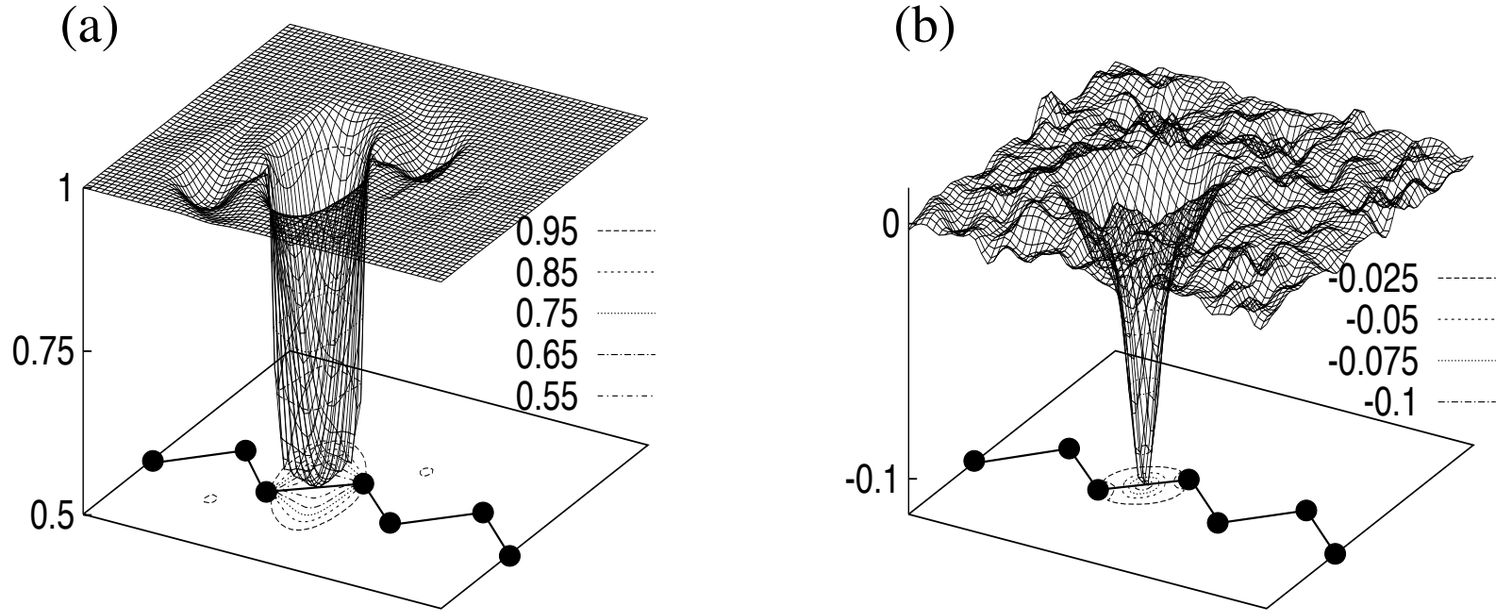
homogeneous electron gas $g_{xc}^{\sigma\sigma'}(r/r_s)$



G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)
P. Gori-Giorgi, F. Sacchetti, G.B. Bachelet, Phys. Rev. B 61, 7353 (2000)

(110) plane of Si, electron at bond center

$g_x^{\mathrm{VMC}}(\vec{r})$ $\qquad$ $g_c^{\mathrm{VMC}}(\vec{r})$



R.Q. Hood, M.Y. Chou, A.J. Williamson, G. Rajagopal, R.J. Needs, W.M.C. Foulkes, Phys. Rev. B 57, 8972 (1998)