antisymmetric wave-functions

(anti)symmetrization of N-body wave-function: N! operations

$$\mathcal{S}_\pm\,\Psi(x_1,\dots,x_N) := \frac{1}{\sqrt{N!}}\sum_P (\pm 1)^P\,\Psi\left(x_{p(1)},\dots,x_{p(N)}\right)$$

antisymmetrization of products of single-particle states

$$\mathcal{S}_-\,\varphi_{\alpha_1}(x_1)\cdots\varphi_{\alpha_N}(x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

much more efficient: scales only polynomially in N

Slater determinant: $\Phi_{\alpha_1\cdots\alpha_N}(x_1,\dots,x_N)$

Slater determinants

$$\Phi_{\alpha_1\cdots\alpha_N}(\mathbf{x}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

simple examples

N=1: $\Phi_{\alpha_1}(x_1) = \varphi_{\alpha_1}(x_1)$

N=2: $\Phi_{\alpha_1\alpha_2}(x) = \frac{1}{\sqrt{2}}\Big(\varphi_{\alpha_1}(x_1)\varphi_{\alpha 2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)\Big)$

expectation values need only one antisymmetrized wave-function:

$$\int d\mathbf{x}\, \overline{(\mathcal{S}_\pm \Psi_a(\mathbf{x}))}\, M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x})) = \int d\mathbf{x} \left(\sqrt{N!}\, \overline{\Psi_a(\mathbf{x})}\right) M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x}))$$

remember: $M(x_1, ..., x_N)$ symmetric in arguments

corollary: overlap of Slater determinants:

$$\int dx_1 \cdots dx_N\, \overline{\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N)}\, \Phi_{\beta_1\cdots\beta_N}(x_1,\ldots,x_N) = \det\Big(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle\Big)$$

basis of Slater determinants

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)} \, \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det\left(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle\right)$$

Slater determinants of ortho-normal orbitals $\varphi_a(x)$ are normalized

a Slater determinant with two identical orbital indices vanishes (Pauli principle)

Slater determinants that only differ in the order of the orbital indices
are (up to a sign) identical

define **convention for ordering indices**, e.g. $\alpha_1 < \alpha_2 < \ldots < \alpha_N$

given K ortho-normal orbitals $\{ \varphi_a(x) \mid \alpha \in \{1, \ldots, K\} \}$

the $K! \,/\, N!\,(K-N)!$ Slater determinants

$$\left\{ \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \,\middle|\, \alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1, \ldots, K\} \right\}$$

are an ortho-normal basis of the N-electron Hilbert space

reduced density-matrices: *p*=1

Laplace expansion

$$\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}(-1)^{1+n}\,\varphi_{\alpha_n}(x_1)\,\Phi_{\alpha_{i\neq n}}(x_2,\ldots,x_N)$$

$$\Gamma^{(1)}(x';x) = \frac{1}{N}\sum_{n,m}(-1)^{n+m}\,\overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_m}(x)\,\frac{\det(\langle\varphi_{\alpha_{j\neq n}}|\varphi_{\alpha_{k\neq m}}\rangle)}{\det(\langle\varphi_{\alpha_j}|\varphi_{\alpha_k}\rangle)}$$

for ortho-normal orbitals

$$\Gamma^{(1)}(x';x) = \sum_n \overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_n(x)|^2$$

reduced density-matrices

expansion of determinant in product of determinants

$$\Phi_{\alpha_1\cdots\alpha_N}(\mathbf{x}) = \frac{1}{\sqrt{\binom{N}{p}}} \sum_{n_1<n_2<\cdots<n_p} (-1)^{1+\sum_i n_i} \Phi_{\alpha_{n_1}\cdots\alpha_{n_p}}(x_1,\ldots,x_p)\,\Phi_{\alpha_{i\notin\{n_1,\ldots,n_p\}}}(x_{p+1},\ldots,x_N)$$

p-electron Slater det   (*N*−*p*)-electron Slater det

express *p*-body density matrix in terms of *p*-electron Slater determinants:

$$\Gamma^{(1)}(x';x) = \sum_n \overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_n(x)|^2$$

$$\Gamma^{(2)}(x_1'x_2';x_1,x_2) = \sum_{n<m} \overline{\Phi_{\alpha_n,\alpha_m}(x_1',x_2')}\,\Phi_{\alpha_n,\alpha_m}(x_1,x_2)$$

$$\text{and} \quad n(x_1,x_2) = \sum_{n,m} |\Phi_{\alpha_n,\alpha_m}(x_1,x_2)|^2$$

in particular

$$n(x_1,x_2) = \sum_{n,m} \left| \frac{1}{\sqrt{2}} \Big(\varphi_{\alpha_n}(x_1)\varphi_{\alpha_m}(x_2) - \varphi_{\alpha_m}(x_2)\varphi_{\alpha_n}(x_1) \Big) \right|^2$$

$$= \sum_{n,m} \Big(|\varphi_{\alpha_n}(x_1)|^2 |\varphi_{\alpha_m}(x_2)|^2 - \overline{\varphi_{\alpha_n}(x_1)}\varphi_{\alpha_m}(x_1)\,\overline{\varphi_{\alpha_m}(x_2)}\varphi_{\alpha_n}(x_2) \Big)$$

exchange hole

pair correlation function for Slater determinant $\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)$

$$g(x_1, x_2) = 1 - \frac{\sum_{n,m} \overline{\varphi_{\alpha_n}(x_1)}\varphi_{\alpha_m}(x_1)\ \overline{\varphi_{\alpha_m}(x_2)}\varphi_{\alpha_n}(x_2)}{n(x_1)\, n(x_2)}$$

homogeneous electron gas: $\varphi_{k\sigma}(x) = \frac{1}{\sqrt{2\pi}} e^{ik\cdot x}\, \chi_\sigma$ with $|k| \leq k_F$

$$g(0,\sigma;r,\sigma) - 1 = -\frac{1}{(n/2)^2}\frac{1}{(2\pi)^6}\int_{|k|,|k'|\leq k_F} d^3k\, d^3k'\, e^{i(k-k')\cdot r}$$

translation invariance
only same spin

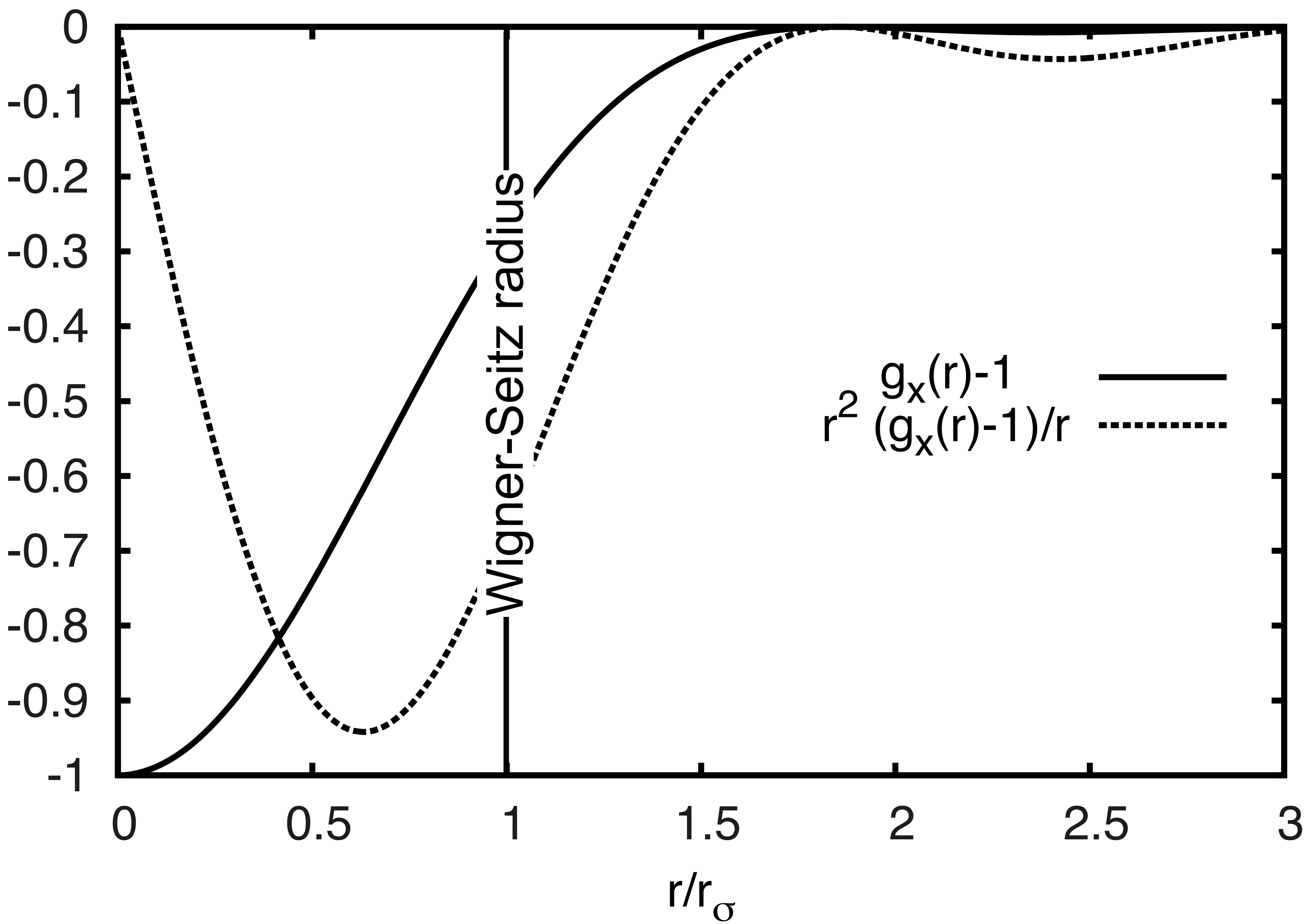
$$= -\left(\frac{3}{4\pi k_F^3}\right)^2 \left|2\pi \int_0^{k_F} dk\, k^2 \int_{-1}^{1} d\cos\theta\, e^{ikr\cos\theta}\right|^2$$

$$= -9\,\frac{\left(\sin(k_F r) - k_F r\cos(k_F r)\right)^2}{(k_F r)^6}$$

exchange hole
for electrons of same spin

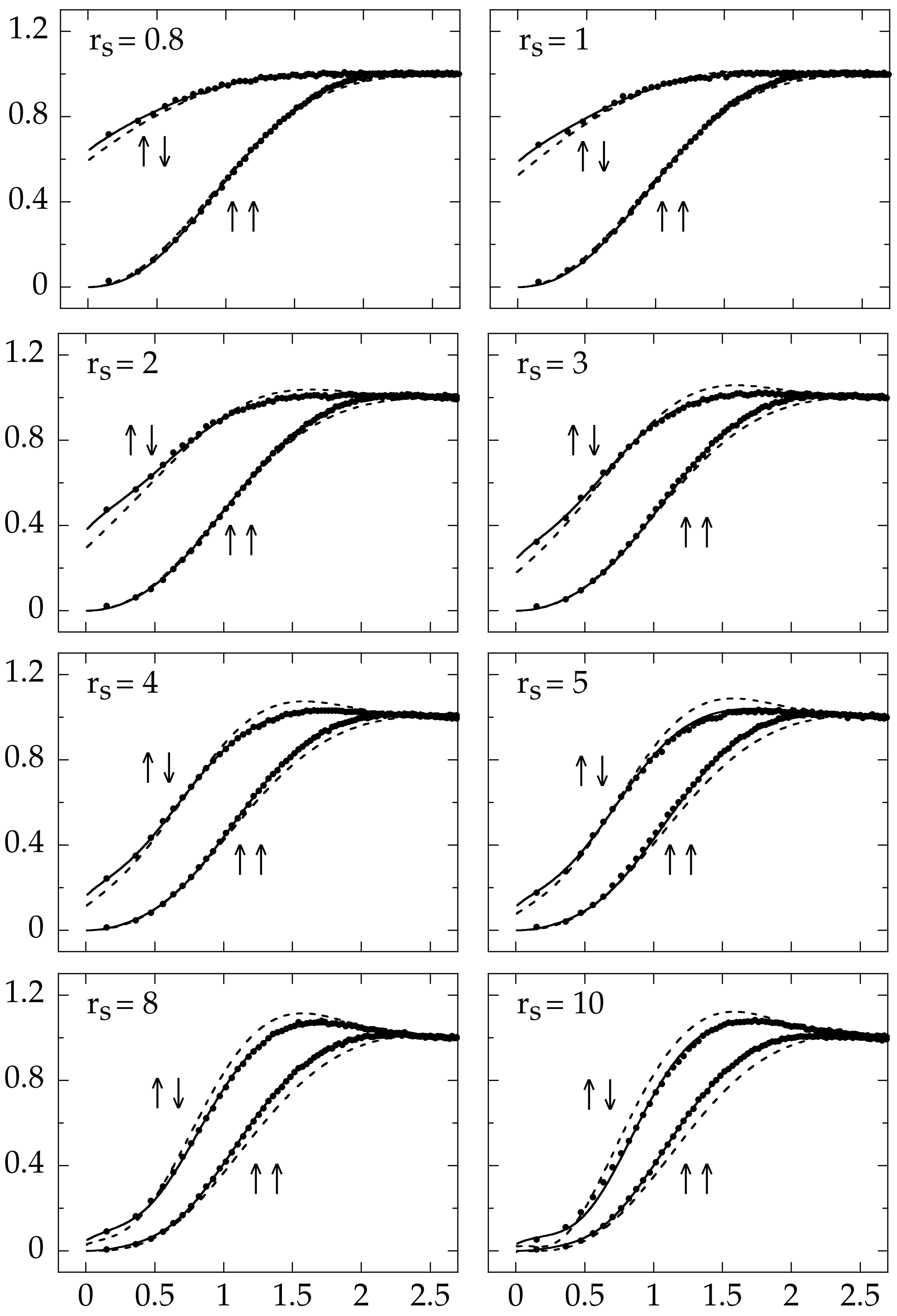
exchange hole

$$g(0,\sigma;r,\sigma)-1=-9\,\frac{\left(\sin(k_F r)-k_F r\cos(k_F r)\right)^2}{(k_F r)^6}$$



exchange-correlation holes from QMC

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



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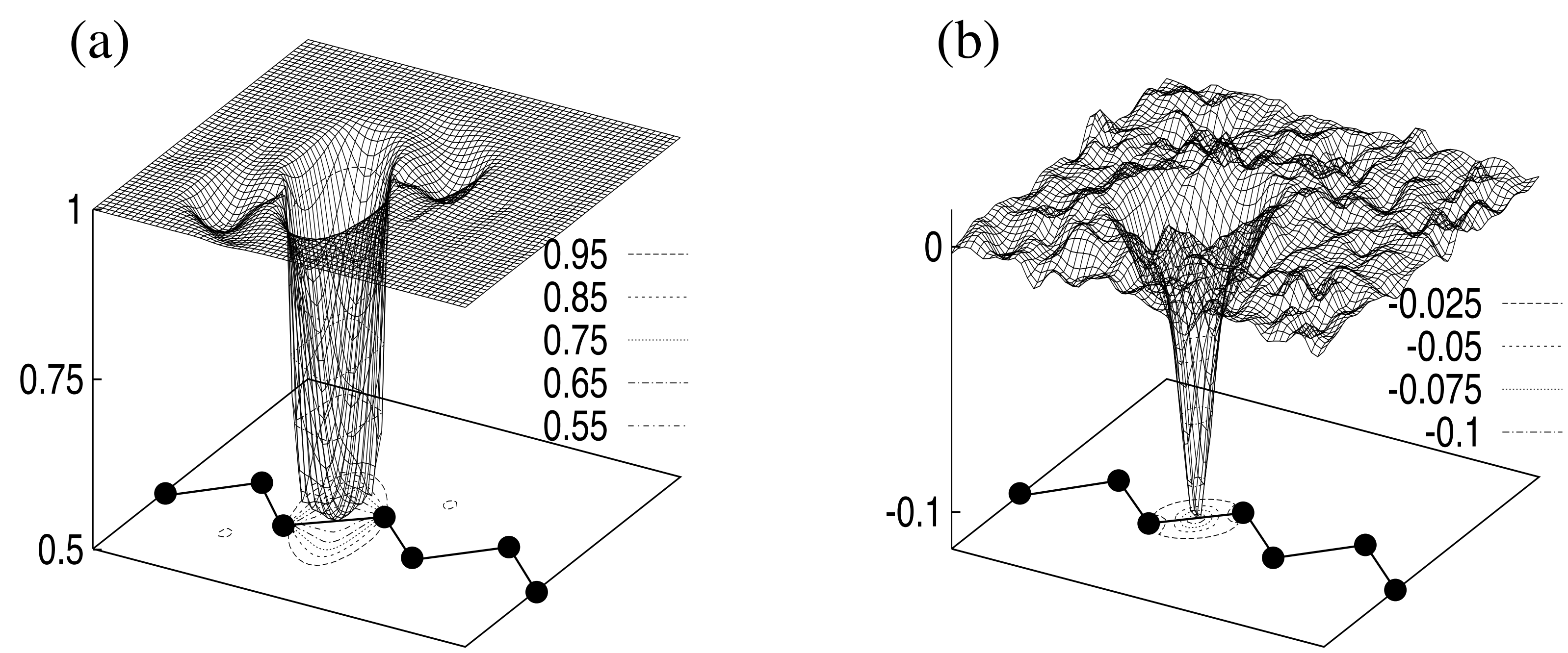
(110) plane of Si, electron at bond center

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



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Slater determinants

Hartree-Fock method:

know how to represent 2-body density matrix derived from Slater determinant

$$\Gamma^{(2)}(x_1' x_2'; x_1, x_2) = \sum_{n<m} \overline{\Phi_{\alpha_n,\alpha_m}(x_1', x_2')}\, \Phi_{\alpha_n,\alpha_m}(x_1, x_2)$$

minimize (á la Coulson)

could generalize reduced density matrices by introducing density matrices for expectation values between different Slater determinants

see e.g. Per-Olov Löwdin, Phys. Rev. **97**, 1474 (1955)

still, always have to deal with determinants and signs.

there must be a better way...