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A natural orbital method for the electron momentum distribution in matter

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Abstract

A variational method for many-electron system is applied to momentum distribution calculations. The method uses a generating two-electron geminal and the amplitudes of the occupancies of one particle natural orbitals as variational parameters. It introduces correlation effects beyond the free fermion nodal structure. © 2000 Elsevier Science Ltd. All rights reserved.

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The characteristics of condensed matter systems are due to the motion and correlation of the electrons [1]. The electron motion can be observed by Compton scattering with photons or by positron annihilation. Recent experiments [2,3] indicate that the momentum density even in simple metals cannot be well represented by a single Slater determinant state. Instead, the momentum density has to be constructed from a correlated state with average occupancies n_i of single particle states in between 0 and 1 [4]. In other words, at the independent particle level there are only N occupancies different from zero, and these are equal to one. When correlation is introduced, we have an infinite number of occupancies different from zero, even though most of them will presumably be very close to zero. The sum rule

$$N = 2 \sum_i n_i \quad (1)$$

remains always true (the factor 2 is due to the spin). The purpose of the present work is to give a simple and efficient calculation method to estimate the occupancies n_i . To simplify the problem, we will consider approximations which neglect the spin. Therefore, the present discussion applies to non-magnetic systems.

If the many-body state is given by the wave function Ψ ,

the first-order density matrix ρ is defined by

$$\rho(\mathbf{r}, \mathbf{r}') = N \int d\xi \Psi^*(\mathbf{r}, \xi) \Psi(\mathbf{r}', \xi). \quad (2)$$

The eigenfunctions ψ_i of ρ , introduced by Löwdin as *natural orbitals* [5] are the most suitable set of one-particle functions to use in this discussion

$$\rho = 2 \sum_i n_i |\psi_i\rangle \langle \psi_i|. \quad (3)$$

The natural orbitals form an orthonormal basis set. Another set of orbitals that are naturally associated with many-body functions are the *generalized overlap amplitudes* [6]. These orbitals are, however, linearly dependent and a canonical orthonormalization of them yields the natural orbitals.

The range of the first-order density matrix $\rho(\mathbf{r}, \mathbf{r}')$ in real space is a fundamental property of quantum mechanical systems since it determines the degree of locality of the bonding properties [7].

The two-particle reduced density matrix σ contains all the information to discuss two-particle interactions V_2 [8,9], and the total energy can be expressed as

$$E[\sigma] = (N/2) \text{Tr}(K\sigma), \quad (4)$$

$$K(\mathbf{r}_1, \mathbf{r}_2) = H_1(\mathbf{r}_1) + H_1(\mathbf{r}_2) + (N-1)V_2(\mathbf{r}_1, \mathbf{r}_2), \quad (5)$$

where H_1 is the one-body part of the hamiltonian. If Ψ is given by single Slater determinant, as in the Hartree–Fock approximation or in the density functional theory [7], then the energy is even determined by a one-particle density

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matrix ρ , such as $\rho = \rho^2$ (idempotency). Recently, Goedecker and Umrigar (GU) [10] proposed to relax the ρ idempotency and to use a natural orbital functional for σ . The GU functional gives still a particular importance to the individual electron picture.

In the present work, an alternative method is explored. One considers the ansatz proposed by Blatt [11–13],

$$\Psi = \text{const} \left[\sum_i g_i a^+(\psi_i^*) a^+(\psi_i) \right]^{N/2} |0\rangle. \quad (6)$$

where $a^+(\psi_i)$ are creation operators of an electron in the state ψ_i . In coordinates space, Ψ is an Antisymmetrized Geminal Product (AGP)

$$\Psi = \text{const Det} |\phi(\mathbf{r}_{i\uparrow}, \mathbf{r}_{j\downarrow})|, \quad (7)$$

where ϕ is single pair wave function, \uparrow is a label for a particle with spin up and \downarrow for a particle with spin down. The size of the determinant is therefore $N/2 \times N/2$. The generating geminal ϕ has a diagonal expansion in the natural orbitals

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\frac{2}{N}} \sum_i g_i \psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_2). \quad (8)$$

In practice, the total energy becomes a functional $E[g_i, \psi_i]$. Thus, g_i and ψ_i are determined by minimizing this functional. Such calculations have been done for some molecules [14]. The Stochastic Gradient Approximation (SGA) optimization [15] is particularly appropriate for the present problem since the variational parameters can be determined avoiding the explicit determination of the total energy.

The AGP is the N particle component of the BCS state [16]. In the limit of N large, the AGP and BCS states become identical. If one set $g_i = v_i/u_i$ with $|u_i|^2 + |v_i|^2 = 1$, then $n_i = |v_i|^2$. Therefore, the electron momentum distribution $n(\mathbf{p})$ is given by the simple formula [17]

$$n(\mathbf{p}) = 2 \sum_i |v_i|^2 |\langle \mathbf{p} | \psi_i \rangle|^2. \quad (9)$$

The expectation value in the AGP of two-particle operators can be found in Ref. [13].

For a two-electron system, the present scheme is equivalent to a configuration interaction calculation and the two-particle reduced density matrix σ is given by a pure state $|\phi\rangle$

$$\sigma = |\phi\rangle\langle\phi|, \quad (10)$$

thus $\sigma = \sigma^2$.

The hydrogen molecule is a good example to illustrate the method. The bonding and antibonding orbitals are

$$\psi_0(\mathbf{r}) = \frac{1}{[2(1+S)]^{1/2}} [f_{\text{R}}(\mathbf{r}) + f_{\text{L}}(\mathbf{r})], \quad (11)$$

$$\psi_1(\mathbf{r}) = \frac{1}{[2(1-S)]^{1/2}} [f_{\text{R}}(\mathbf{r}) - f_{\text{L}}(\mathbf{r})], \quad (12)$$

where $f_{\text{R,L}} = \sqrt{\alpha^3/\pi} e^{-\alpha|r-R_{\text{R,L}}|}$ are 1s atomic orbitals, S is the

overlap integral (varying from 0 to 1) and α is a variational parameter (varying from 1 to 1.66). The two-body wave function ϕ can be approximately given by

$$\phi(\mathbf{r}, \mathbf{r}') = g_0 \psi_0(\mathbf{r}) \psi_0(\mathbf{r}') + g_1 \psi_1(\mathbf{r}) \psi_1(\mathbf{r}'). \quad (13)$$

Then

$$g_0 = \frac{1}{\sqrt{2}} \left[1 + \frac{\kappa}{\sqrt{1+\kappa^2}} \right]^{1/2}, \quad (14)$$

$$g_1 = -\frac{1}{\sqrt{2}} \left[1 - \frac{\kappa}{\sqrt{1+\kappa^2}} \right]^{1/2}, \quad (15)$$

where κ is a function of S and of the integrals

$$U = \langle f_{\text{L}} f_{\text{L}} \left| \frac{1}{r_{12}} \right| f_{\text{L}} f_{\text{L}} \rangle, \quad (16)$$

$$V = \langle f_{\text{L}} f_{\text{R}} \left| \frac{1}{r_{12}} \right| f_{\text{L}} f_{\text{R}} \rangle, \quad (17)$$

$$t = \langle f_{\text{L}} f_{\text{L}} \left| \frac{1}{r_{12}} \right| f_{\text{L}} f_{\text{R}} \rangle, \quad (18)$$

$$J = \langle f_{\text{L}} f_{\text{L}} \left| \frac{1}{r_{12}} \right| f_{\text{R}} f_{\text{R}} \rangle. \quad (19)$$

For large d , $S \approx 0$, $\kappa = 2t/(U - V)$. Therefore, when $d \rightarrow \infty$, $g_0 = -g_1 = 1/\sqrt{2}$ and

$$\phi(\mathbf{r}, \mathbf{r}') = g_0 (f_{\text{R}}(\mathbf{r}) f_{\text{L}}(\mathbf{r}') + f_{\text{L}}(\mathbf{r}) f_{\text{R}}(\mathbf{r}')). \quad (20)$$

This means that the correlation effects derive the electrons back on their own atoms like in the Heitler-London ansatz.

For the linear chain molecule H_4 , the $|\psi_i\rangle (i = 0, 1, 2, 3)$, have i nodes. In momentum space, $\langle \mathbf{p} | \psi_0 \rangle$ is peaked at $p = 0$, but the $\langle \mathbf{p} | \psi_i \rangle$ (for $i = 1, 2, 3$) are peaked at higher momenta. When d is small, only $|\psi_0\rangle$ and $|\psi_1\rangle$ are occupied, while, in the limit $d \rightarrow \infty$, the SGA method yields $g_0 = g_1 = -g_2 = -g_3$. In the Hartree-Fock approximation [18], the momentum density $n(p)$ of the chain H_{32} is more similar to that of a free-electron gas, with a given Fermi momentum p_{F} , rather than that of the hydrogen atom. However, when the occupation number can vary, one expects $n(p)$ to develop high momentum tails. Recent experiments probing the electron momentum distribution in simple metals [2,3] have observed similar tails.

The Homogeneous Electron Gas (HEG) is another interesting limit for solids. In this system, the plane waves are the natural orbitals and the total energy per particle $\varepsilon = E/N$ is a function of the density parameter r_s (i.e. the radius of the volume taken by one electron). The difference between the interacting and free HEG momentum densities for different r_s yields the Lam-Platzman correction [20] within the density functional theory.

Csányi and Arias [21] computed the GU energy functional in the HEG and minimized the result with respect to the occupancy $n(k)$. At high density (small r_s), the result seems to reproduce the correct RPA limit and $n(k)$ has a

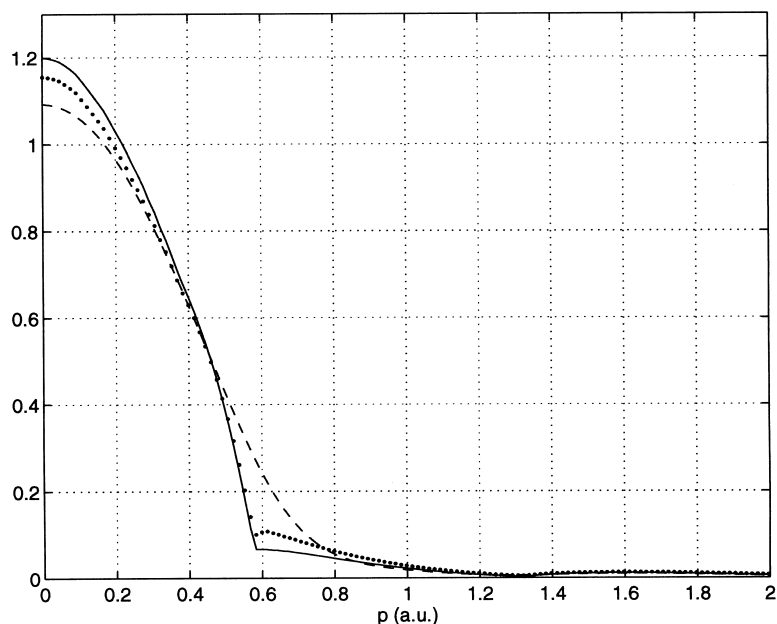


Fig. 1. Total valence-electron Compton profiles of Li along (1 0 0). The solid line is the LDA calculation, the dotted line is the LDA with Lam–Platzman corrections and the dashed line is the AGP with $|\Delta(\mathbf{k})| = 0.1$ a.u.

Daniel–Vosko like momentum dependence [22]. However, when $r_s = 1$, one finds $\epsilon = 0.546$ (a.u.), while the Diffusion Quantum Monte Carlo gives $\epsilon = 0.596$ (a.u.) [19]. This is quite a surprising result, since a variational result should be always greater than the exact energy. The reason is that the two-particle reduced density matrix σ has been varied over too large class of functions: the restriction to N -representable σ has not been imposed. In other words, one cannot find a many-body state yielding this σ . The AGP is by definition N -representable. Therefore, it provides a general variational scheme for many-electron system. When the AGP is applied to the interacting (with Coulomb repulsion) HEG, one finds the independent particle occupation [23]. However, correlation effects in the particle occupation may appear in a more realistic inhomogeneous electron system.

Recently, the electron momentum density of Li has attracted a particular attention since an experimental work by Schükle et al. [24] suggests an anomalously small Fermi break. However, Quantum Monte Carlo simulations [25], GW calculations by Eguluz et al. [26] and the density functional theory with the Lam–Platzman correction (shown in Fig. 1) do not support this anomaly at the FS. One possible reason is that all these methods use many-body wave functions within the free fermion nodal structure.

It is therefore worthwhile to investigate schemes beyond the free fermion nodal structure like the AGP. In solid Li one can approximate the natural orbitals by the Kohn–Sham orbitals [4] and do the following BCS ansatz for the

occupation amplitudes [27,28]

$$g(\mathbf{k}) = \frac{\Delta(\mathbf{k})}{\epsilon(\mathbf{k}) + \sqrt{\epsilon^2(\mathbf{k}) + \Delta^2(\mathbf{k})}}. \quad (21)$$

The band energy $\epsilon(\mathbf{k})$ is zero at the Fermi level and $\Delta(\mathbf{k})$ can be either calculated variational or fitted to the experiment. Fig. 1 shows that important correlation effects can be observed in the Li Compton profile if $|\Delta(\mathbf{k})|$ is about 0.1 a.u. Strikingly these effects appear to be in good agreement with the difference LDA-experiment shown in the paper by Schükle et al. [24, Fig. 3]. One important message to be drawn from this example is that the momentum distribution is much more sensitive to the nodes of the many-body function than the electron density in real space.

In conclusion, the present paper presents a total energy functional of natural orbitals. The method goes beyond the Slater determinant nodal structure. For two-electron systems, it is equivalent to a configuration interaction calculation. It can capture important correlation effects in the electron momentum density calculation. The knowledge of these effects is crucial for a proper interpretation of the experimental spectra.

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