A natural orbital method for the electron momentum distribution in matter

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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.

The characteristics of condensed matter systems are due to the motion and correlation of the electrons. The electron motion can be observed by Compton scattering with photons or by positron annihilation. Recent experiments indicate that the momentum density in real space is a fundamental property of quantum mechanical systems since it determines the degree of locality of the bonding properties.

The two-particle reduced density matrix \( \sigma \) contains all the information to discuss two-particle interactions \( V_2 \) and the total energy can be expressed as

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

where \( H_1 \) is the one-body part of the hamiltonian. If \( \Psi \) is given by single Slater determinant, as in the Hartree-Fock approximation or in the density functional theory, then the energy is even determined by a one-particle density matrix \( \rho \), such as \( \rho = \rho^2 \) (idempotency). Recently, Goedecker and Umrigar (GU) proposed to relax the \( \rho \) idempotency and to use a natural orbital functional for \( \sigma \). 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

\[
\Psi = \text{const Det}[\phi(r_i - r_j)].
\]

The generating geminal \( \phi \) has a diagonal expansion in the natural orbitals

\[
\phi(r_1, r_2) = \sqrt{\frac{2}{N}} \sum_i g_i \psi_i^*(r_1) \psi_i(r_2).
\]

In practice, the total energy becomes a functional \( E[g_i, \psi_i] \). Thus, \( g_i \) and \( \psi_i \) are determined by minimizing this functional. Such calculations have been done for some molecules. The Stochastic Gradient Approximation (SGA) optimization 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 the BCS state [7]. 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 $u_i = |u_i|^2$. Therefore the electron momentum distribution $n(p)$ is given by the simple formula [7]

$$n(p) = 2 \sum_i |v_i|^2 |<p|\psi_i>|^2.$$  \hspace{1cm} (9)

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

For a 2 electron system, the present scheme is equivalent to a configuration interaction calculation and the two-particle reduced density matrix \(\sigma\) is given by a pure state \(|\phi\rangle\)

$$\sigma = |\phi><\phi|,$$  \hspace{1cm} (10)

thus \(\sigma = \sigma^2\).

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

$$\psi_0(r) = \frac{1}{[2(1+S)]^{1/2}}[f_R(r) + f_L(r)],$$  \hspace{1cm} (11)

$$\psi_1(r) = \frac{1}{[2(1-S)]^{1/2}}[f_R(r) - f_L(r)],$$  \hspace{1cm} (12)

where \(f_{R,L} = \sqrt{\alpha}e^{\alpha r-R_{R,L}}\) are 1s atomic orbitals, \(S\) is the overlap integral (varying from 0 to 1) and \(\alpha\) is a variational parameter (varying from 1 to 1.66). The two-body wave function \(\phi\) can be approximated by

$$\phi(r,r') = g_0\psi_0(r)\psi_0(r') + g_1\psi_1(r)\psi_1(r').$$  \hspace{1cm} (13)

Then

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

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

where \(\kappa\) is a function of \(S\) and of the integrals

$$U = <f_Lf_L | \frac{1}{r_{12}} | f_Lf_L>,$$  \hspace{1cm} (16)

$$V = <f_Lf_R | \frac{1}{r_{12}} | f_Lf_R>,$$  \hspace{1cm} (17)

$$t = <f_Lf_L | \frac{1}{r_{12}} | f_Lf_R>,$$  \hspace{1cm} (18)

$$J = <f_Lf_L | \frac{1}{r_{12}} | f_Rf_R>.$$  \hspace{1cm} (19)

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

$$\phi(r,r') = g_0(f_R(r)f_L(r') + f_L(r)f_R(r')).$$  \hspace{1cm} (20)

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

For the linear chain molecule \(H_4\), the \(\mid\psi_i\rangle\) (\(i = 0, 1, 2, 3\)), have \(i\) nodes. In momentum space, \(<p|\psi_0\rangle\) is peaked at \(p = 0\), but the \(<p|\psi_i\rangle\) (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 [8], 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 [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 [21] 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 the occupancy \(n(k)\). At high density (small \(r_s\)), the result seems to reproduce the correct RPA limit and \(n(k)\) has a Daniel-Vosko like momentum dependence [22]. However when \(r_s = 1\), one finds \(\varepsilon = 0.546\) (a.u.), while the Diffusion Monte Carlo gives \(\varepsilon = 0.596\) (a.u.) [13]. This is a quite surprising result, since a variational result should be always greater than the exact energy. The reason is that the two-particle reduced density matrix \(\sigma\) has been varied over too large class of functions: the restriction to \(N\)-representable \(\sigma\) has not been imposed. In other words, one cannot find a many-body state yielding this \(\sigma\). 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 an inhomogeneous electron gas.

A crucial question is whether or not the fixed node approximation, used by the Quantum Monte Carlo (QMC) simulations, gives a significant momentum density error.
in realistic extended systems. A recent QMC calculation for solid Li\cite{24} corrects about 30\% the discrepancy between the experimental Compton profiles\cite{2} and the density functional result. The fixed node approximation might be a cause of the remaining discrepancy. The Lam-Platzman correction, which is in the same nodal structure, gives a similar result (see Fig. 1).

![FIG. 1. Total valence-electron Compton profiles of Li along (1 0 0).](image)

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\cite{4} and do the following BCS ansatz for the occupation amplitudes\cite{25,26}

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

The band energy $\epsilon(k)$ is zero at the Fermi level and $\Delta(k)$ can be either calculated variationally or fitted to the experiment. Fig. 1 shows that important correlation effects can be observed in the Li Compton profile if $|\Delta(k)|$ is about 0.1 a.u..

In conclusion, the present paper presents a total energy functional of natural orbitals. The method goes beyond the Slater determinant nodal structure. For 2 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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