INTRODUCTION TO THE VARIATIONAL DENSITY MATRIX METHOD AND ITS APPLICATION TO DENSE HYDROGEN

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Abstract: A new variational principle for optimizing thermal density matrices is introduced. As a first application, the variational many body density matrix is written as a determinant of one body density matrices which are approximated by Gaussians with the mean, width and amplitude as variational parameters. This variational density matrix is used to calculate properties of the hot, dense hydrogen. First results for a density of $r_s = 2$ are presented.

1 INTRODUCTION

In this paper, we present a computational approach for systems with non-degenerate electrons analogous to the methods used for ground state many body computations. Although this represents an oversimplification, we may usefully view the ground state computations as consisting of three levels of increasing accuracy. At the first level, the ground state wave function consists of determinants, for both spin species, of single particle orbitals often taken from local density functional theory. If desired, additional correlations may be included by multiplying the above wave function by a Jastrow factor. Finally, diffusion Monte Carlo methods using the nodes of this wave function to avoid the Fermion problem may be used to calculate the exact correlations consistent with the nodal structure.

The finite temperature theory proceeds similarly. Rather than the ground state wave function, a thermal density matrix

$$\rho(\mathbf{R},\mathbf{R}';\beta) = \left\langle \mathbf{R}|e^{-\beta\mathcal{H}}|\mathbf{R}'\right\rangle = \sum_s e^{-\beta E_s}\Psi_s(\mathbf{R})\Psi_s(\mathbf{R}') \tag{1}$$

is needed to compute the thermal averages of operators

$$\langle \mathbf{O}\rangle = \frac{\mathrm{Tr}\,[\mathbf{O}\rho]}{\mathrm{Tr}\,[\rho]}\ . \tag{2}$$

At the first level, this many body density matrix may be approximated by determinants of one-body density matrices, for both spin types, as well as the ions

$$\rho(\mathbf{R},\mathbf{R}';\beta) = \begin{vmatrix} \rho_1(\mathbf{r}_1,\mathbf{r}_1';\beta) & \dots & \rho_1(\mathbf{r}_N,\mathbf{r}_1';\beta) \\ \dots & \dots & \dots \\ \rho_1(\mathbf{r}_1,\mathbf{r}_N';\beta) & \dots & \rho_1(\mathbf{r}_N,\mathbf{r}_N';\beta) \end{vmatrix} \tag{3}$$

Again, additional correlations may be introduced with a temperature dependent Jastrow factor. Finally, the nodal structure from this variational density matrix (VDM) may be used in restricted path integral Monte Carlo (RPIMC). This method has been extensively applied using the free particle nodes. One aim of the present work is to provide more realistic nodal structures as input to RPIMC.

In this work, we can only briefly sketch the derivation of the VDM method. For details on the derivation as well as on the VDM properties, see article [1]. We propose solving the Bloch equation by parameterizing the density matrix with a set of parameters q_i depending on imaginary time β and $\mathbf{R}'$,

$$\rho(\mathbf{R},\mathbf{R}';\beta) = \rho(\mathbf{R},q_1,\dots,q_m) \quad \text{where} \quad q_i(\mathbf{R}';\beta) \tag{4}$$

The following variational principle is then introduced to determine the parameters

$$\int \left(\frac{\partial \rho(\mathbf{R},\mathbf{R}';\beta)}{\partial \beta} + \mathcal{H}\, \rho(\mathbf{R},\mathbf{R}';\beta) \right)^2 d\mathbf{R} = 0 \quad . \tag{5}$$

This reveals the imaginary-time equivalent to the approach of Singer and Smith [2] for an approximate solution of the time dependent Schrödinger equation using wave packets. From this variational principle, the fundamental set of first order differential equations for the dynamics of the variation parameters in imaginary time follows

$$\frac{1}{2}\frac{\partial H}{\partial \vec{q}} + \overset{\leftrightarrow}{\mathcal{N}}\ \dot{\vec{q}} = 0 \quad \text{where} \quad H \equiv \int \rho \mathcal{H} \rho \, d\mathbf{R} \tag{6}$$

and the norm matrix

$$\mathcal{N}_{ij} = \lim_{q' \to q} \frac{\partial^2 N}{\partial q_i \partial q'_j} \quad \text{with} \quad N \equiv \int \rho(\mathbf{R}, \vec{q}; \beta)\; \rho(\mathbf{R}, \vec{q}\,'; \beta)\; d\mathbf{R} \ . \tag{7}$$

These equations are general and no particular ansatz including the type of spin statistics has been specified.

For hot, dense hydrogen, we approximate the single particle density matrix in Eq. 3 as a Gaussian with the mean $\mathbf{m}$, squared width w and amplitude factor d,

$$\rho_1(\mathbf{r}, \mathbf{r}', \beta) = (\pi w)^{-3/2} \exp\left\{ -\frac{1}{w}(\mathbf{r} - \mathbf{m})^2 + d \right\} \tag{8}$$

as variational parameters. The initial conditions at $\beta \longrightarrow 0$ are $w = 2\beta$, $\mathbf{m} = \mathbf{r}'$ and $d = 0$ in order to regain the correct free particle limit. In the absence of a potential the exact free particle density matrix is recovered. The harmonic oscillator case is also correct since the Gaussian approximation is exact there. At low temperature, the VDM as a function of $\mathbf{r}$ goes to the ground state wave function, which is given by the Rayleigh-Ritz variational principle. This property follows from Eq. 5 for any ansatz.

We will study hydrogen at a density of $r_s = 2$ in the temperature range of $5000\,$K$\leq$T$\leq 250\,000\,$K. While treating the ions classically, we represent the many body density matrix for the electrons as a product of determinants, one for each spin state, built from Gaussian single particle density matrices. Applying this antisymmetric ansatz to the variational principle in Eq. 5 leads to N! terms in the differential equations for the dynamics of the variation parameters. In the parameter range of temperature and density, it was found to be sufficient to consider only the pair exchange terms of the kinetic energy [1]. This level of approximation was also used in the real time wave packet dynamics [3, 4]. It is stressed that, unlike the real time computations, the full determinantal form is then used in calculating the various averages.

2 MANY PARTICLE MONTE CARLO SIMULATIONS

We model hydrogen by 32 protons and 32 electron in a cubic cell. The thermal averages in Eq. 2 are computed using a Monte Carlo simulation in configuration space. For each configuration, the variational parameters are determined by solving Eq. 6.

The average squared width of the Gaussian as a function of temperature is shown in Fig. 1. At high temperature, the width approaches the free particle limit. This is an advantage over the real time wave packet dynamics where the width is known to grow without limits [5, 6]. At low temperature, the attraction to the protons dominate, which leads to a decreasing average width. Finally, bound states form and the average width approaches a finite limit. At this density, this is well below the ground state squared width of the isolated molecule, $3.138\, a_0^2$.

A comparison of the pair correlation functions (PCF) from VDM and PIMC [7] is shown in Fig. 2. At the density of consideration $r_s = 2$, a fairly good agreement is found. However, a detailed analysis of the density dependency remains to be made.

For temperatures below $20\,000\,$K, a peak in the proton-proton PCF emerges at $1.4 a_0$ that clearly demonstrates the formation of molecules.

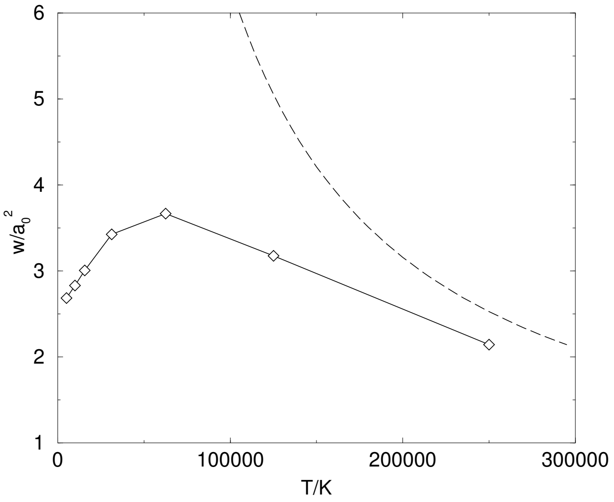

Figure 1: Average squared width of the Gaussian single particle density matrices as a function of temperature at the density of $r_s = 2$ (solid line) compared to the free particle value (dashed line).

In the proton-electron PCF, one finds a strong attraction present even at high temperatures such as $250\,000\,$K. At low temperatures, the electrons are bound in atoms and molecules. This PCF does not show a clear distinction between the two cases. The comparison with PIMC shows that VDM underestimates the height of the peak significantly, which is a result of the Gaussian ansatz that does not satisfy the cusp condition at the proton.

The same spin electron-electron PCF shows the effect of the Pauli exclusion principle leading to a strong repulsion of electrons. This effect is not present in the interaction of electrons with anti-parallel spin, which leads to a significantly different PCF. At high temperature, one observes the effect of the Coulomb repulsion. At low temperature, one finds a peak at the origin that is a result of the formation of molecules, in which two electrons of opposite spin are localized along the bond. This dominates over the repulsive forces.

Summarizing this brief description one can say that the VDM approach provides a way to systematically improve the many particle density matrix. Already the simplest ansatz using one Gaussian gives a good description of hydrogen at $r_s = 2$ in the discussed temperature range. Further one can use this essentially analytic density matrix to derive the nodal surface in RPIMC simulations, replacing the free particle nodes by a density matrix that already covers the principle physical effects.

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References

[1] B. Militzer and E. L. Pollock. in preparation.

[2] K. Singer and W. Smith. *Mol. Phys.*, **57**(4):761–775, 1986.

[3] D. Klakow, C. Toepffer, and P.-G. Reinhard. *J. Chem. Phys.*, **101**:10766, 1994.

[4] W. Ebeling and B. Militzer. *Phys. lett. A*, **226**:298, 1997.

[5] B. Militzer. *Quanten-Molekular-Dynamik von Coulomb-Systemen.* Logos publishing company, Berlin, 1996.

[6] M. Knaup, P.-G. Reinhard, and C. Toepffer. *Contrib. Plasma Phys.*, **39** 1-2:57, 1999.

[7] W. R. Magro, D. M. Ceperley, C. Pierleoni, and B. Bernu. *Phys. Rev. Lett.*, **76**:1240, 1996.

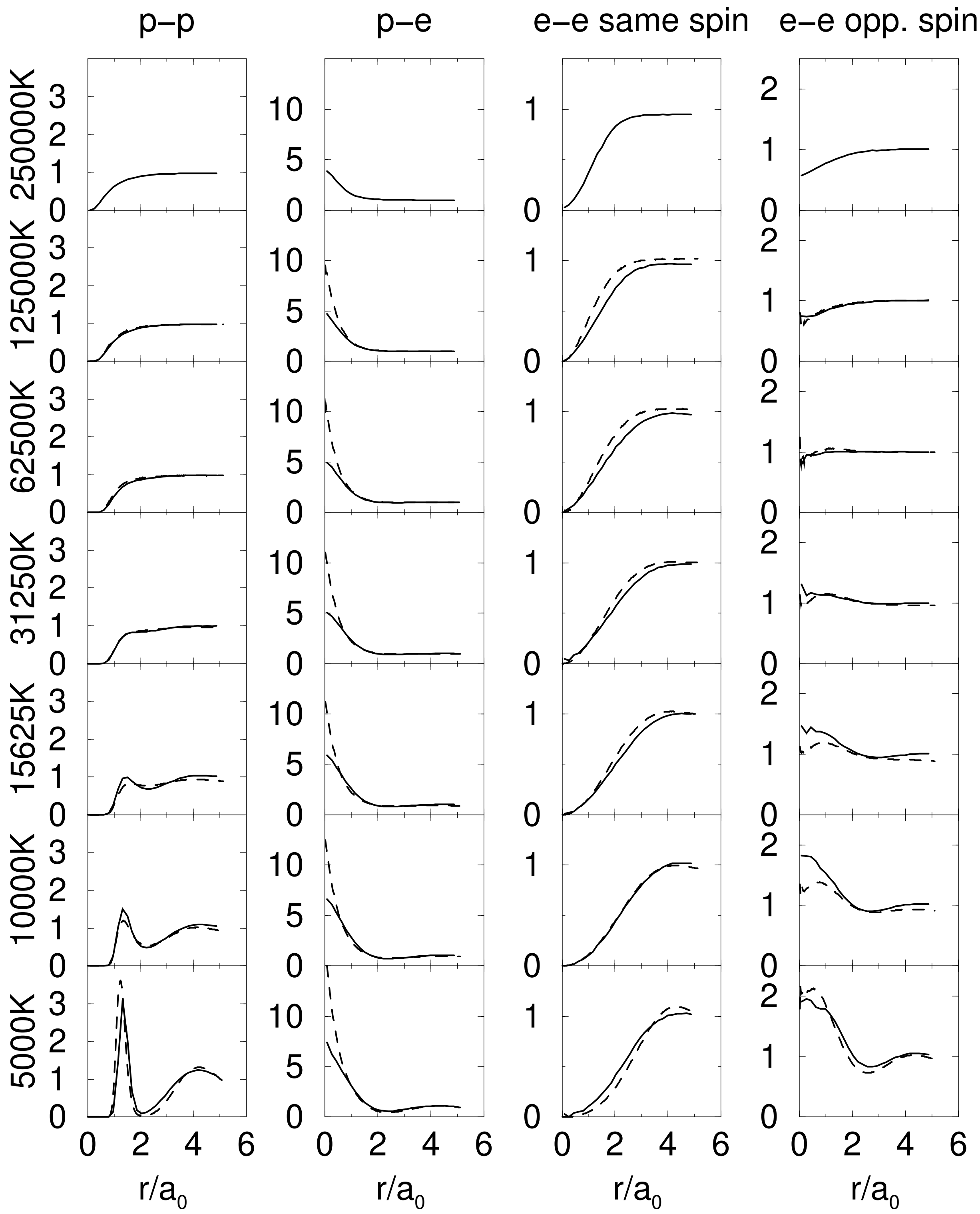

Figure 2: The pair correlation functions of hydrogen derived from VDM simulations for a density of $r_s = 2$ (solid lines). The columns show the proton-proton, proton-electron, same spin and opposite spin electron-electron pair correlation functions. The rows correspond to different temperatures. Results from PIMC simulations [7] are included for the six lowest temperatures (dashed lines).