Our ansatz is:

$$\Psi_T(R) = \exp(-\sum_{i<j} U_{s_i s_j}(|r_i - r_j|))\mathrm{Det}(\phi_k(r_\ell)) \quad (2)$$

where s_i represents the type of particle i (electron or proton), r_i the coordinates of particle i, $U_{st}(r)$ the pseudopotential between pairs of particles of types s and t and $\phi_k(r)$ the kth occupied single particle orbital. For the electrons in the metal phase, the orbitals we have used are plane waves (exp[ikr]) where k lies inside the Fermi sea ($k \leq k_F$). These are satisfactory orbitals for the electron gas and are expected to be also accurate for metallic hydrogen since the band is half filled and from perturbation theory one expects the effects of the underlying proton lattice will not be felt near the center of the Brillouin zone. The lattice periodicity appears in the electron-proton pseudopotential. For protons and for electrons in the molecular phase, the orbitals used are Gaussians centered around a set of crystal lattice sites $\{Z_k\}$, i.e., $\exp[-C_s(r - Z_k)^2]$. The lattice used in the calculations reported here is FCC. We are also exploring the use of Wannier functions as electron orbitals.

Reasonable approximations to the pseudopotentials $U_{st}(r)$ can be obtained from a local energy argument using the random phase approximation as was done in ref. (6) for jellium. The Fourier transforms of these pseudopotentials to lowest order in the ratio of electron to proton mass, γ, are:

$$\begin{aligned} 2U_{ee}(k) &= -1 + (1 + a_k)^{1/2} \\ 2U_{ep}(k) &= -a_k(1 + a_k)^{-1/2} \qquad (3) \\ 2U_{pp}(k) &= (a_k/(1 + a_k)/\gamma)^{1/2} \end{aligned}$$

Where $a_k = 12r_s/k^4$, k is in units of a^{-1}, $a = (4\pi n/3)^{-1/3}$, n is the electron density, $r_s = a/a_0$, and a_0 is the Bohr radius. The electron-electron pseudopotential is identical to that used for jellium and is known to be close to the optimal.[7] These functions have the correct cusp conditions at r = 0 and hence remove the infinities in the local energy when $r_i = r_j$. In addition for large r or small k they have the correct behavior because the random phase approximation is exact in that limit.

Shown in Table I are result of fixed-node simulations for several densities for a system of 108 atoms on a FCC lattice. Periodic boundary conditions and Ewald image potential are used to eliminate surface effects. A correction, identical to that made for jellium, has been made to eliminate the remaining finite size effects. The first two columns represent the total energy/particle in Rydbergs for a static lattice, E_S, (where the protons are infinitely massive and hence have no kinetic energy) and with the proper proton mass, E_H. The statistical error is approximately 10^{-3} Ry. The difference in these two energies is then the zero point energy of the protons. Also shown in Table I are three representative theoretical calculations for a static lattice; correlated basis-function theory (E_{CBP}),[8] many-body perturbation theory (E_{PERT})[9] and local density functional theory (E_{LDF}).[8]

The numbers reported here are preliminary. Further studies are needed to judge the effects of the assumed nodal structure, the underlying lattice and of a finite-size system. However, the accuracy appears to be an order of magnitude better than current theoretical approaches and can be used to benchmark them. The simulation method is uniquely advantageous for studying phase transitions as the procedure is identical in all phases. Work is now in progress to locate the dissociation and metallization transitions and to study the rotational ordering in the molecular solid.

TABLE I

r_s	E_s	E_H	E_{CBF}	E_{PERT}	E_{LDF}
1.0	-0.726	-	-	-0.719	-
1.13	-0.892	-0.856	-0.903	-0.884	-0.906
1.31	-1.002	-0.974	-1.017	-0.996	-1.021
1.45	-1.033	-1.013	-1.054	-1.032	-1.059
1.61	-1.053	-	-1.069	-1.044	-1.074
1.77	-1.050	-1.036	-1.068	-	-1.073

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THE CALCULATION OF THE PROPERTIES OF METALLIC HYDROGEN USING MONTE CARLO*

D. M. Ceperley
National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 USA
B. J. Alder
Lawrence Livermore National Laboratory
University of California
Livermore, California 94550 USA

The application of Monte Carlo to hydrogen at zero temperature is discussed. The trial function is a generalization of the pair product type used for jellium. Preliminary results for the metallic phase are given.

Bulk hydrogen at low temperature is the simplest experimentally available quantum many-body system. Because of its prevalence in the universe, its possible high temperature superconductivity and its importance in laser fusion, much theoretical and experimental effort has been directed towards its properties at high pressure.[1] However such basic properties as the equation of state above 100 Kbar and the metallization density are not substantially improved over the calculations of Wigner and Huntington.[2]

Monte Carlo has proven to be a reliable computational tool for computing ground state properties of many-body systems. Whitlock, et al.,[3] have achieved agreement with experimental results of liquid and solid Helium 4. Recently, these exact Monte Carlo methods have been generalized to many-fermion systems. The present authors have calculated the correlation energy of the jellium and its low density phase transitions.[4-5] Hydrogen affords the chance of computing the properties of a real many-body system ab initio. Only the Coulomb potential, and the nonrelativistic Schroedinger equation are assumed. Both electrons and protons are fully quantum mechanical: no Born-Oppenheimer, or harmonic lattice approximation need be made. Let us first briefly review the solution of the Schroedinger equation via a stochastic computer simulation.

The Schroedinger equation written in imaginary time is a diffusion equation in 3N dimensions (N is the number of particles). To make the diffusion process computationally stable and efficient, a trial function $\Psi_T(R)$ is used. After multiplying by Ψ_T, the Schroedinger equation can be written in the form:

$$-\frac{\partial f}{\partial t} = \sum_{i=1}^{N} \frac{\hbar^2}{2m_i} [-\nabla_i^2 f + \nabla_i (f \nabla_i \ln|\Psi_T|^2)] + [\Psi_T^{-1} H \Psi_T - E_0] f \qquad (1)$$

Here H is the Hamiltonian and E_0 the ground state energy. It is easily verified that at large times $f(R,t) \rightarrow \Psi_T(R)\phi_0(R)$ where $\phi_0(R)$ is the desired exact ground state eigenfunction. Eq. (1) has a simple interpretation as a stochastic process. An ensemble of systems is constructed at $t = 0$ from the probability distribution $|\Psi_T(R)|^2$. Each member of the ensemble is then advanced in time with three separate processes corresponding respectively to the terms of eq. (1): i) random diffusion, ii) drift by the trial force, and iii) branching. By branching, it is meant, that a particular system is either eliminated from or duplicated in the ensemble depending on the value of the local energy $E_L(R) \equiv \Psi_T^{-1}H\Psi_T$. The effect of Fermi statistics can be accounted for in an approximate though realistic way by eliminating systems from the ensemble when they cross the nodes of $\Psi_T(R)$. We refer to this as the 'fixed-node' procedure. The value of E_0 in Eq. (1) necessary to stabilize the ensemble population will be a rigorous and accurate upper bound to the exact Fermi energy. The exact eigenvalue may be estimated by allowing systems to cross nodes and account for antisymmetry by carrying along a sign with the system. The algorithms are described in more detail in refs. (4-5). The computation of the properties of the many-body wavefunction has thus been reduced to finding an accurate, though simple, trial wavefunction and a sufficiently powerful computer, as these are the two factors which limit the accuracy of method.

Here we discuss our calculation of the metallic, monatomic phase of hydrogen. A satisfactory trial function can be obtained by generalizing the Bijl-Dingle-Jastrow-Slater or pair product function to a multicomponent system.

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