**Ab-initio** molecular dynamics for high-pressure liquid Hydrogen

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We introduce an efficient scheme for the molecular dynamics of electronic systems by means of quantum Monte Carlo. The evaluation of the (Born-Oppenheimer) forces acting on the ionic positions is achieved by two main ingredients: i) the forces are computed with finite and small variance, which allows the simulation of a large number of atoms, ii) the statistical noise corresponding to the forces is used to drive the dynamics at finite temperature by means of an appropriate friction matrix. A first application to the high-density phase of Hydrogen is given, supporting the stability of the liquid phase at \(\approx 300\text{GPa}\) and \(\approx 400K\).

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The phase diagram of Hydrogen at high pressure is still under intense study from the experimental and theoretical point of view. In particular in the low temperature high-pressure regime there is yet no clear evidence of a metallic atomic solid, and a suggestion was given in Ref.\(^[2]\) that the liquid phase is instead more stable. Indeed, for high pressures around 300GPa, a two fluid (proton and electron) superconducting phase of the conventional type, namely induced by the strong electron-phonon coupling, has been conjectured\(^\text{[2]}\). In this work we use an improved ab-initio molecular dynamics (AMD) by using accurate forces computed by Quantum Monte Carlo (QMC). We present preliminary results, showing that the liquid phase is energetically more stable, due to the strong electron correlation, at least within the Resonating Valence Bond (RVB) variational approach\(^[1]\), which is very accurate also in the solid phase.

AMD is well established as a powerful tool to investigate many-body condensed matter systems. Indeed, previous attempts to apply Quantum Monte Carlo (QMC) for the dynamics of ions\(^[4]\) or for their thermodynamic properties\(^[5]\) are known, but they were limited to small number \(N\) of electrons or to total energy corrections of the AMD trajectories, namely without the explicit calculation of the forces.

**Calculation of forces with finite variance.** The simplest method for accurate calculations within QMC, is given by the so called variational Monte Carlo (VMC), which allows to compute the variational energy expectation value \(E_{VMC} = \frac{\langle \psi_T | H | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle}\) of a highly accurate correlated wave function (WF) \(\psi_T\) by means of a statistical approach: electronic configurations \(\{x\}\), with given electron positions \(\vec{r}_i\) and spins \(\sigma_i = \pm 1/2\) for \(i = 1, \cdots N\), are usually generated by the Metropolis algorithm according to the probability density \(\mu_x \propto \psi_T(x)^2\). Then \(E_{VMC}\) is computed by averaging statistically over \(\mu_x\) the so called local energy \(e_L(x) = \frac{\langle \psi_T | H | x \rangle}{\langle \psi_T | x \rangle}\), namely \(E_{VMC} = \int d\mu_x \ e_L(x)\), where \(\int d\mu_x\) indicates conventionally the \(3N\) multidimensional integral over the electronic coordinates weighted by \(\psi_T^2(x)\). In the present work we assume that the WF \(\psi_T(x) = \langle x | \psi_T \rangle = J \times \det A\) is given by a correlated Jastrow factor \(J\) times a determinant \(D\) of a \(N \times N\) matrix \(A\), such as for instance a Slater determinant. The main ideas of this approach can be straightforwardly generalized to more complicated and more accurate WF’s.

The efficient calculation of the energy derivatives, namely the forces \(\vec{f}_{R_i} = - \frac{\partial E_{VMC}}{\partial \vec{R}_i}\), for \(i = 1, \cdots N_A\), where \(N_A\) is the number of atoms, is the most important ingredient for the AMD. Within VMC they can be computed by simple differentiation of \(E_{VMC}\), using that not only the Hamiltonian \(H\) but also \(\psi_T\) depend explicitly on the atomic positions \(\vec{R}_i\). This leads to two different contributions to the force \(\vec{f}_{R_i} = \vec{f}_{R_i}^{HF} + \vec{f}_{R_i}^P\), the Hellmann-Feynman \(\vec{f}_{R_i}^{HF}\) and the Pulay one \(\vec{f}_{R_i}^P\), where:

\[
\vec{f}_{R_i}^{HF} = - \int d\mu_x \ \langle x | \partial_{\vec{R}_i} H | x \rangle \tag{1}
\]
\[
\vec{f}_{R_i}^P = - 2 \int d\mu_x \ (e_L(x) - E_{VMC}) \partial_{\vec{R}_i} \log |\psi_T(x)| \tag{2}
\]

However in order to obtain a statistically meaningful average, namely with finite variance, some manipulations are necessary because the first integrand may diverge when the atoms are close to some electronic positions, whereas the second integrand is analogously unbounded when a configuration \(x\) approaches the nodal surface determined by \(\psi_T(x) = 0\). By defining with \(d(\delta)\) the distance of \(x\) from the nodal region (the minimum electron-atom distance), \(e_L(x), \partial_{\vec{R}_i} \log |\psi_T(x)| \simeq 1/d\) \((\langle x | \partial_{\vec{R}_i} H | x \rangle \simeq 1/d^2)\), whereas \(\mu_x \simeq d^2\) \((\mu_x \simeq \delta^2)\), leading to an unbounded integral of the square integrand in Eq.(2) (Eq.1), namely to *infinite variance*. The infinite variance problem in Eq.\(^1\) was solved in several ways. Here we adopt a very elegant and efficient scheme proposed by Caffarel and Assaraf\(^\text{[6]}\). Instead the infinite variance problem in Eq.(2) was not considered so far, and this is clearly a problem for a meaningful definition of ionic AMD consistent with QMC forces.

In this letter we solve this problem in the following
simple way, by using the so called re-weighting method. We use a different probability distribution \( \mu'_x \propto \psi_G(x)^2 \), determined by a guiding function \( \psi_G(x) \):

\[
\psi_G(x) = R'(x)\left(\psi_T(x)/R(x)\right)
\]

where \( R(x) \propto \psi_T(x) \to 0 \) for \( d \to 0 \) is a "measure" of the distance from the nodal surface \( \psi_T(x) = 0 \). By assumption \( \psi_T \) may vanish only when \( \det A = 0 \) and therefore \( R(x) \) is chosen to depend only on \( A \). For reasons that will become clear later on we have adopted the following expression:

\[
R(x) = 1/\sqrt{\sum_{i,j=1}^{N}|A^{-1}|^2}.
\]

Then the guiding function is defined by properly regularizing \( R(x) \), namely:

\[
R'(x) = \begin{cases} 
R(x) & \text{if } R(x) \geq \epsilon \\
\epsilon(R(x)/\epsilon)^{R(x)/\epsilon} & \text{if } R(x) < \epsilon.
\end{cases}
\]

The non obvious regularization for \( R(x) < \epsilon \) instead of e.g. \( R'(x) = \text{Max}[\epsilon, R(x)] \) was considered in order to satisfy the continuity of the first derivative of \( \psi_G(x) \) when \( R(x) = \epsilon \), thus ensuring that \( \psi_G(x) \) remains as close as possible to the trial function \( \psi_T \). In this way the Metropolis algorithm can be applied for generating configurations according to a slightly different probability \( \mu'(x) \) and the exact expression of \( \bar{f}_R^p \) can be obtained by the so called umbrella average:

\[
\bar{f}_R^p = -2\int d\mu'_x S(x)(\partial_{\bar{R}})^{-2}S(x)
\]

Now, the re-weighting factor \( S(x) = (\psi_T(x)/\psi_G(x))^2 = \text{Min}[1,(R(x)/\epsilon)^2] \propto d^2 \), cancels out the divergence of the integrand, that was instead present in Eq. (3). Hence the mentioned integrands in the numerator and denominator of Eq. (5) represent bounded random variables and have obviously finite variance. In this way the problem of infinite variance is definitely solved within this simple re-weighting scheme. Moreover, in the present method \( R(x) \) is not related to an overall factor of the total WF, such as the total determinant, defined in a very wide range of values \( \simeq \epsilon \) over the various configurations. It is instead obtained by using a quantity \( \bar{R}(x) \propto \psi_G(x) \) with small fluctuations. Therefore the present scheme is particularly efficient and stable also for large \( N \).

We show in Fig. 1 a comparison of several methods for computing the Pulay force component acting on a Hydrogen proton at \( r_s = 1.31 \) in a bcc lattice. As it is clear in the plot for the \( N = 128 \) case, the difference between a method with finite variance and the standard one with infinite variance is evident. Moreover for \( N = 250 \) the simpler choice \( R(x) = |\det A| \) with finite (but large) variance is clearly very inefficient due to the difficulty to cross from the region with \( R(x) < \epsilon \), where the integrand almost vanishes (see Fig. 1), to the one with \( R(x) > \epsilon \) and viceversa. Instead in the present scheme an appropriate choice of \( \epsilon \), such that \( \int d\mu_x S(x) \simeq 1/2 \), allows frequent barrier crossings any few Metropolis steps also for large \( N \). In this way the \( 3N_A \times 3N_A \) correlation matrix \( \alpha_{QMC} \), defining the statistical correlation between the force components, can be efficiently evaluated:

\[
\alpha_{QMC} = \left< \bar{f}_{\bar{R}} - \bar{f}_{\bar{R}} \right> = \left< \bar{f}_{\bar{R}} - \bar{f}_{\bar{R}} \right> >
\]

where the brackets \(< \> \) indicate the statistical average over the QMC samples. The correlation matrix \( \alpha_{QMC} \), that within the conventional method is not even defined, will be a fundamental ingredient for a consistent AMD with QMC forces and therefore the solution of the infinite variance problem is particularly important for this purpose.

**FIG. 1:** (color online). Evolution of the integrand in Eq. (6) as a function of the Monte Carlo iterations. Each new sample is obtained after 2\( N \) Metropolis trials.

**Langevin dynamics.** In the following derivation we assume that ions have unit mass, that can be generally obtained by e.g. a simple rescaling of lengths for each ion independently. For clarity and compactness of notations, we also omit the ionic subindices \( i \) when not explicitly necessary. Moreover matrices (vectors) are indicated by a bar (arrow) over the corresponding symbols, and the matrix-vector product is also implicitly understood. We start therefore by the following AMD equations for the ion coordinates \( \bar{R} \) and velocities \( \bar{\upsilon} \):

\[
\bar{\upsilon} = -\gamma(\bar{R})\bar{\upsilon} + \bar{f}(\bar{R}) + \bar{\eta}(t)
\]

\[
\bar{\bar{R}} = \bar{\upsilon}
\]

By using the fluctuation-dissipation theorem the friction matrix \( \gamma(\bar{R}) \) is related to the temperature \( T \) (henceforth the Boltzmann constant \( k_B = 1 \)) by the relation:

\[
\gamma(\bar{R}) = \frac{1}{2T} \alpha(\bar{R})
\]
where $\tilde{\alpha}(\tilde{R})$ is generally a symmetric correlation matrix:
\[
< \tilde{\eta}_i(t)\tilde{\eta}_j(t') > = \delta(t-t')\tilde{\alpha}(\tilde{R}).
\] (11)

It is important to emphasize that, as a remarkable generalization of the standard AMD used in [7], in the present approach the friction matrix $\tilde{\gamma}$, may depend explicitly on the ion positions $\tilde{R}$, so that Eq. (10) can be satisfied even for a generic correction matrix $\tilde{\alpha}(\tilde{R})$. In fact, since forces are computed by QMC, we can assume that there exists also a QMC contribution to $\tilde{\alpha}(\tilde{R})$:
\[
\tilde{\alpha}(\tilde{R}) = \tilde{\alpha}_0 + \Delta_0 \tilde{\alpha}_{QMC}(\tilde{R})
\] (12)
where $\Delta_0 > 0$ and $\tilde{\alpha}_0$ is the identity matrix $I$ up to another positive constant $\alpha_0$, $\tilde{\alpha}_0 = \alpha_0 I$.

**Integration of the Langevin dynamics.** In the interval $t_n - \frac{\Delta t}{2} < t < t_n + \frac{\Delta t}{2}$, for $\Delta t$ small, the positions $\tilde{R}$ are changing a little and, within a good approximation, we can neglect the $\tilde{R}$ dependence in the RHS of Eq. (8).

Moreover the velocities $\tilde{v}_n$ are computed at half-integer times $t_n - \frac{\Delta t}{2}$, whereas coordinates $\tilde{R}_n$ are assumed to be defined at integer times $\tilde{R}_n = \tilde{R}(t_n)$. Then the integration of Eq. (8) in the mentioned intervals can be recast in the following useful form, where the force components are corrected by appropriate noisy vectors:
\[
\tilde{\eta} = \frac{\tilde{\gamma}}{2 \sinh(\frac{\Delta t}{2} \tilde{\gamma})} \int_{t_n - \frac{\Delta t}{2}}^{t_n + \frac{\Delta t}{2}} dt e^{\tilde{\gamma}(t-t_n)} \tilde{\eta}(t)
\] (16)

By using that $\tilde{\alpha} = 2T\tilde{\gamma}$ from Eq. (10), the correlator defining the discrete (time integrated) noise $\tilde{\eta}$ can be computed explicitly and is given by:
\[
< \tilde{\eta}_i \tilde{\eta}_j > = 2T^2 \frac{\sinh(\Delta t \tilde{\gamma})}{\sinh(\frac{\Delta t}{2} \tilde{\gamma})^2} = \tilde{\alpha}^t
\] (17)

This means that the QMC noise has to be corrected in a non trivial way as explained in the following.

**Noise correction.** The QMC noise is given during the simulation, and therefore in order to follow the correct dynamics another noise $\tilde{\eta}_{\text{ext}}$ has to be added to the noisy force components in a way that the total integrated noise is the correct expression $\tilde{\eta} = \tilde{\eta}_{\text{ext}} + \tilde{\eta}_{\text{QMC}}$. By using that the QMC noise in Eq. (7) is obviously independent of the external noise, we easily obtain the corresponding correlation matrix:
\[
< \tilde{\eta}_{i \text{ext}} \tilde{\eta}_{j \text{ext}} > = \tilde{\alpha}^t - \tilde{\alpha}_{\text{QMC}}
\] (18)

On the other hand, after substituting the expression $\tilde{\gamma} = \frac{1}{\tilde{T}} \left( \alpha_0 + \Delta_0 \tilde{\alpha}_{\text{QMC}} \right)$ and using the expression (17) for $\tilde{\alpha}^t$, we finally obtain a positive definite matrix in Eq. (15) for $\Delta t \lesssim \Delta_0$ [8]. Hence $\tilde{\eta}^\text{ext}$ is a generic Gaussian correlated noise that can be easily sampled by standard algorithms. After that the random vector $\tilde{\eta}^\text{ext}$ is added to the force $\tilde{f} + \tilde{\eta}_{\text{QMC}}$ obtained by QMC, and replaces $\tilde{f} + \tilde{\eta}$ in Eq. (13). This finally allows to obtain an accurate AMD with a corresponding small step error. In our approach the choice $\alpha_0 = 0$ is also allowed but, following Refs. [7,9], much better performances of the AMD are obtained with non zero $\alpha_0 > 0$ and/or $\Delta_0 > \Delta t$, namely with an external noise larger than the smallest possible one ($\alpha_0 = 0, \Delta_0 = \Delta t$). The main advantage of this technique is that, at each iteration, by means of Eq. (10), the statistical noise on the total energy and forces (see Fig. 2) can be much larger than the target temperature $T$, and this allows to improve the QMC efficiency by several orders of magnitude.

**Optimization of the WF.** In the following examples we use a variational WF $\mathbf{J} \times \text{det } A$ that is able to provide a very accurate description of the correlation energy, due to a particularly efficient choice of the determinant factor, that allows to describe the RVB correlations [10, 11]. The Jastrow factor $\mathbf{J}$ used here depends both on the charge and spin densities, for a total of $N_A^2$ variational parameters. We employ periodic boundary conditions; for each proton we use two periodic gaussians centered at each ionic position, whereas for the Jastrow we use only one Gaussian. As it is shown in the table, the accuracy of our WF is remarkable. Indeed the small difference between the so called DMC -providing the lowest accuracy of our calculation, as well as that the $N=54$ is an accidental closed shell, and will not be considered in the forthcoming analysis.

In order to optimize the WF we use the recent method introduced in Ref. [12], devised here in an appropriate way to optimize a large number of parameters during the AMD simulation. At each iteration time $t_n$ we compute the generalized energy gradients $\mathbf{g}_n = \tilde{s}^{-1} \frac{\partial E_{\text{MC}}}{\partial \beta}$, where $\tilde{s}$ is the reduced overlap matrix between the logarithmic WF derivatives, appropriately regularized as in

**TABLE I:** Comparison of the total energy per proton (Hartree) for Hydrogen in the bcc lattice at $t_e = 1.31$ compared with the published ones with lowest energy (to our knowledge). All energies are in Hartree.

| $N$ | $E_{\text{VMC}}/N_A$ | $E_{\text{VMC}}/N_A$ | $E_{\text{DMC}}/N_A$ | $E_{\text{DMC}}/N_A$ |
|-----|---------------------|---------------------|---------------------|---------------------|
| 16  | -0.49875(3)         | -0.49878(1)         | -0.49164(4)         | -0.4905(1)          |
| 54  | -0.53573(2)         | -0.5353(2)          | -0.53805(4)         | -0.5390(5)          |
| 128 | -0.49495(1)         | -0.49472(2)         | -0.49663(3)         | -0.4978(4)          |
| 250 | -0.49740(2)         | -0.49923(2)         | -0.49740(2)         | -0.49923(2)         |
Application to high-pressure Hydrogen. The phase diagram of Hydrogen is still under debate especially for a possible stable low temperature ≃ 400K high pressure (≃ 300GPa) liquid phase. We show in Fig. the evolution of the internal energy and corresponding temperature as a function of time with the proposed AMD with QMC forces, starting from the bcc solid at \( r_s = 1.31 \). This solid is clearly unstable because, even at \( \approx 1300K \) the internal energy decreases by a huge quantity (about 0.02H per proton). Although we have not studied the possible stability of all other solid phases yet, the internal energy obtained with VMC at the lowest temperature appears slightly lower than the ground state energy of all plausible solid phases even when estimated by the DMC method. This is rather remarkable because the application of DMC to our variational states certainly decreases their energies, and also that our ground state energy is certainly below the computed internal energy at finite temperature.

In conclusion we have shown that it is possible to make a realistic and accurate simulation of many atoms consistently with QMC forces, for a time (≃ 1ps) comparable with the present ab-initio methods based on DFT. The first important outcome of this calculation is that the bcc solid structure appears clearly unstable even at low temperatures \( (N = 16 \) and \( N = 128 \) are consistent, suggesting small size effects in this phase), where a molecular liquid with explicit pairing correlations absent in the metallic solid phase, has much lower internal energy. This liquid phase represents either a RVB Mott insulator or a non conventional superconductor, stabilized only by the strong electron correlation. It is clear that more systematic and accurate studies are necessary to clarify this novel scenario, especially on the experimental side.

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