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Integrated Quantum/Classical Modeling of Hydrogenic Materials

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Final LDRD Report on Project #3504460000
Integrated Quantum/Classical Modeling of Hydrogenic Materials

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Abstract

Path integral Monte Carlo simulations and calculations were performed on molecular hydrogen liquids. The equation-of-state, internal energies, and vapor liquid phase diagrams from simulation were found to be in quantitative agreement with experiments. Analytical calculations were performed on H_2 liquids using integral equation methods to study the degree of localization of the hydrogen molecules. Very little self-trapping or localization was found as a function of temperature and density. Good qualitative agreement was found between the integral equation calculations and the quantum Monte Carlo simulations for the radius of gyration of the hydrogen molecules. Path integral simulations were also performed on molecular hydrogen on graphite surfaces, slit pores, and in carbon nanotubes. Significant quantum effects on the adsorption of hydrogen were observed.

I. Introduction

Because of its light mass, the motion of hydrogen and other small nuclei frequently need to be modeled quantum mechanically. A measure of the importance of quantum effects is given by the de Broglie wavelength λ defined as $\lambda^2 = \frac{\hbar^2}{kTm}$ where m is the mass of the particle, $\hbar$ is Planck's constant divided by 2π , k is Boltzmann's constant, and T is the absolute temperature. For the hydrogen molecule the de Broglie wavelength ($\lambda \approx 1.6 \text{ \AA}$ at 10 K and $0.3 \text{ \AA}$ at 298 K) is small but not insignificant for temperatures even up to room temperature. Johnson and coworkers¹ have shown that quantum effects have a significant influence on the equation-of-state and the phase diagram of H_2 liquids. The purpose of this program was to develop the computational tools to model the statistical mechanics of hydrogen and other light nuclei.

There are several methods available for treating the finite temperature quantum motion problem. These include quantum corrections to classical properties through perturbation theory, quantum Monte Carlo methods, and the path integral formalism. Perturbation corrections to classical properties are inaccurate except in the very weakly quantum limit. While quantum Monte Carlo explicitly accounts for exchange effects, it is computationally demanding and the accuracy is limited by the choice of the trial wave functions. The path integral method is formally exact, and can achieve virtually any desired accuracy in practice. For this reason we have chosen to employ the path integral method in this work.

The path integral formalism is based on the isomorphism discovered by Feynman between a quantum particle and a classical ring polymer. This isomorphism allows us to build upon existing molecular dynamics (MD) and Monte Carlo (MC) codes already

available for studying classical problems. We note that for the problems of interest in this study the molecules may be treated as distinguishable (Boltzmann statistics). It has previously been shown that quantum exchange effects can safely be ignored for liquid hydrogen. Algorithms exist, however, to include exchange in path integral calculations and can be implemented if necessary.

The model system chosen for study in this program was taken to be the hydrogen molecular liquid and gas. This system was chosen because quantum effects are known to be important. Furthermore, hydrogen is of great practical importance in many Sandia programs ranging from hydrogen in metals and isotope separation for defense applications to hydrogen storage in porous media for energy programs. In this work we will study H_2 liquids both in the bulk phase and also adsorbed on surfaces.

In this report we will begin with a brief discussion of the theoretical underpinnings of the path integral formulation of quantum statistical mechanics. We will then show specific applications of the theory to study the equation-of-state and phase behavior of H_2 using computer simulation. This will be followed by an analytical, integral equation approach that exploits the quantum/classical isomorphism. Monte Carlo simulation will then be employed to study the adsorption of H_2 molecules on substrates. Finally we conclude this report by discussing a novel MD approach for solving quantum statistical mechanics problems that exploits massively parallel computation methods.

II. Theoretical Background

All the thermodynamic properties of a system of N quantum particles in thermal equilibrium are obtainable from the density matrix $\rho(\bar{R}, \bar{R}'; \beta)$ defined as

$$\begin{aligned}\rho(\vec{R}, \vec{R}'; \beta) &= \langle \vec{R} | e^{-\beta H} | \vec{R}' \rangle \\ &= \sum_i \phi_i^*(\vec{R}) \phi_i(\vec{R}') e^{-\beta E_i}\end{aligned}\quad (2.1)$$

where H is the Hamiltonian operator, $\vec{R} = \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$ specifies the positions of the N particles in phase space, $\phi_i(\vec{R})$ are the N -body wave functions with energy states E_i and $\beta = 1/kT$. The expectation value of some operator O can then be computed as

$$\begin{aligned}\langle O \rangle &= \text{Tr}(O \cdot \rho) \\ &= Z^{-1} \int d\vec{R} d\vec{R}' \rho(\vec{R}, \vec{R}'; \beta) \delta(\vec{R} - \vec{R}')\end{aligned}\quad (2.2)$$

where Z is the partition function and is related to the density matrix according to

$$\begin{aligned}Z &= \text{Tr}(\rho) \\ &= \int \rho(\vec{R}, \vec{R}; \beta) d\vec{R}\end{aligned}\quad (2.3)$$

Unfortunately the density matrix is exceedingly hard to evaluate in this form and is essentially an intractable problem for all but the simplest of problems. Great progress can be made, however, by exploiting the isomorphism between a system of quantum particles and a classical system of Gaussian polymer rings. To see this isomorphism one begins by recognizing that the density matrix can be written as an integral over a number $p-1$ of intermediate states³

$$\rho(\bar{R}_0, \bar{R}_p; \beta) = \int \dots \int d\bar{R}_1 \dots d\bar{R}_{p-1} \rho(\bar{R}_0, \bar{R}_1; \tau) \dots \rho(\bar{R}_{p-1}, \bar{R}_p; \tau) \quad (2.4)$$

where τ is a timestep equal to β/p . We now make use of the Trotter approximation³ that permits us to write

$$\exp(-\tau H) \approx \exp(-\tau K) \exp(-\tau V) \quad (2.5)$$

where K and V are the kinetic energy and potential energy operators. This approximation allows us to factor the density matrix into kinetic and potential parts

$$\rho(\bar{R}_0, \bar{R}_2; \tau) \approx \int d\bar{R}_1 \langle \bar{R}_0 | e^{-\tau K} | \bar{R}_1 \rangle \langle \bar{R}_0 | e^{-\tau V} | \bar{R}_1 \rangle \quad (2.6)$$

Since normally the potential energy of the system depends only on the interatomic distances we find that the potential operator part reduces to

$$\langle \bar{R}_1 | e^{-\tau V} | \bar{R}_2 \rangle = e^{-\tau V} \delta(\bar{R}_2 - \bar{R}_1) \quad (2.7)$$

The kinetic energy part of the density matrix can be evaluated by solving the problem of N free quantum particles in a cubic box. This leads to³

$$\langle \bar{R}_0 | e^{-\tau K} | \bar{R}_1 \rangle = (4\pi\lambda\tau^{-3N/2}) \exp\left[-\frac{(\bar{R}_0 - \bar{R}_1)^2}{4\lambda\tau}\right] \quad (2.8)$$

Thus, using Eqs. (2.4)-(2.8) we can write the density matrix in the form

$$\rho(\bar{\mathbf{R}}_0, \bar{\mathbf{R}}_p; \beta) = \int \dots \int d\bar{\mathbf{R}}_1 \dots d\bar{\mathbf{R}}_{p-1} (4\pi\lambda\tau)^{-3Np/2} \exp \left\{ - \sum_{m=1}^p \left[\frac{(\mathbf{R}_{m-1} - \mathbf{R}_m)^2}{4\lambda\tau} \right] + \tau V(\bar{\mathbf{R}}_m) \right\} \quad (2.9)$$

This can be recognized by inspection to correspond to the partition function for a system of classical, Gaussian chains of p particles connected by harmonic springs having a spring constant equal to $p/2\lambda^2$. Since for the purposes of calculating averages we only require the diagonal part of the density matrix $\rho(\bar{\mathbf{R}}, \bar{\mathbf{R}}; \beta)$ the quantum problem maps to the classical polymer ring (ie. $\bar{\mathbf{R}}_0 = \bar{\mathbf{R}}_p$). In the limit as the number of beads approaches infinity, the mapping becomes exact. This is the famous Feynman isomorphism between quantum and classical statistical mechanics.

III. Molecular Hydrogen

Hydrogen molecules in the condensed state were modeled by representing the quantum hydrogen molecules as classical polymer rings consisting of beads labeled $i=1,2,\dots,p$. Each bead represents the H_2 molecule at a different imaginary time. In the quantum/classical isomorphism, interactions between molecules corresponds to polymer rings that interact only between beads having the same index or time. We use the Silvera-Goldman potential⁴, a potential that is known to be accurate for hydrogen molecules

$$v(r) = \exp(\alpha - \beta r - \gamma r^2) - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_9}{r^9} + \frac{C_{10}}{r^{10}} \right) f_c(r) \quad (3.1)$$

The first term in the potential in Eq. (3.1) accounts for the repulsive interactions whereas the second term represents long range attractive interactions. $f_c(r)$ is a damping function designed to turn off the attractions at short distances given by

$$\begin{aligned} f_c(r) &= \exp\left[-\left(r/r_c - 1\right)^2\right] & r < r_c \\ &= 1 & r \geq r_c \end{aligned} \quad (3.2)$$

The potential parameters in atomic units for H_2 are as follows: $\alpha=1.713$, $\beta=1.5671$, $\gamma=0.00993$, $C_6=12.14$, $C_8=215.2$, $C_9=143.1$, $C_{10}=4813.9$, and $r_c=8.321$.

A path integral hybrid Monte Carlo method¹ (PIHMC) was used for simulation of polymer rings in both the NVT and NPT ensembles to compute the equation-of-state and internal energy of hydrogen. PIHMC was used in a Gibbs ensemble to model the vapor-liquid phase behavior of H_2 . PVT results¹ for fluid hydrogen are shown in figure 1. It can be seen from this figure that quantitative agreement is found between simulation and the experimental PVT data⁵. Since Eq. (3.1) is a spherical representation of H_2 we added vibrational and rotational energy contributions using standard methods¹ to the translational internal energy obtained from the PIHMC simulation to obtain the total internal energy of the system. A comparison¹ between the simulation and experiment for the internal energy is given in figure 2. It can be seen that there is excellent agreement between simulation and experiments⁵.

Figure 1 – Fluid H_2 density as a function of temperature. The lines represent experimental data⁵ and the symbols are from the PIHMC simulations¹.

Figure 2 – Total internal energy for H_2 as a function of temperature at 20 MPa. The line is experimental data⁵ and the points are from the simulations¹.

It can be seen from figures 1 and 2 that the quantum Monte Carlo simulations give virtually quantitative agreement for thermodynamic properties of hydrogen in the liquid state. An interesting question to ask is: how important are the quantum effects in these simulations? This is addressed in figure 3 where the Gibbs free energy is shown for H_2 from both quantum and classical simulations.

Figure 3 – The Gibbs free energy of H_2 as a function of temperature at 10.0 MPa. The line is experimental data⁵, the circles from quantum simulations¹, and the squares from classical simulations¹.

It can be seen that quantum effects are significant up to at least 60° K at a pressure of 10 MPa.

The complete vapor liquid phase diagram can be obtained from quantum Monte Carlo simulations in a Gibbs ensemble. Results¹ from these calculations are shown in figure 4.

Figure 4 – The vapor – liquid phase diagram for H_2 . The circles are from Monte Carlo simulations¹, the line is from an empirical equation-of-state⁶, and the diamonds are from experimental data⁵.

The agreement between simulation and experiment is seen to be very good.

IV. Integral Equation Theory

Thus far in this report we have discussed the treatment of quantum liquids with Monte Carlo simulation. We will now discuss an analytical treatment first developed by Chandler and coworkers^{7,8}. Since the quantum problem is equivalent to the classical polymer ring liquid, we can apply the PRISM theory⁹ of Curro and Schweizer, originally developed for polymer liquids, to this problem. Because of the peculiar nature of the interactions in which only beads of the same index (or imaginary time) interact with each other, each bead must be considered as independent or inequivalent in PRISM theory. We can get around this complication, however, by making the adiabatic approximation, appropriate for weakly quantum systems. In this approximation we treat the quantum liquid as a single polymer ring in a bath of classical particles. Such an approximation

would be expected to be valid for H_2 molecules where quantum effects are of intermediate strength. With this approximation, the problem simplifies because now the beads on the ring can be treated as equivalent with each bead interacting with the remaining classical particles in the system. This is illustrated schematically in figure 5.

Figure 5

In order to test the adiabatic approximation PIHMC simulations were performed on H_2 at a series of temperatures and densities. The radius of gyration from the full simulations are compared with the corresponding adiabatic simulations in Table 1.

Table 1 – Comparison between the exact quantum simulations of H_2 and simulations using the adiabatic approximation

Temperature (°K)	$\langle R_g \rangle$ (Å) Exact	$\langle R_g \rangle$ (Å) Adiabatic
Density = 42 mol/l		
20	.498	.474
30	.396	.405
40	.354	.360
60	.309	.297
100	.249	.228

200	.165	.165
300	.135	.135

Density=30 mol/l

20	.519	.501
30	.435	.420
40	.378	.372
60	.315	.303
100	.228	.231
200	.159	.165
300	.138	.135

Density=20 mol/l

40	.360	.375
50	.405	.336
60	.309	.306
70	.294	.282
80	.282	.267
90	.255	.252
100	.234	.240

Within the errors of the Monte Carlo simulation, the radius of gyration of the exact and adiabatic calculations are the same.

We now focus our attention on the behavior of the hydrogen ring polymer response (or self-pair correlation function) $\omega_p(r, t - t')$ and the hydrogen solvent radial distribution function $g_{ps}(r)$. These are defined as

$$\omega_p(r, t - t') = \langle \delta[\bar{r}(t) - \bar{r}(t')] \rangle, \quad 0 \leq t \leq \beta\hbar \quad (4.1)$$

and

$$g_{ps}(r) = \rho_s^{-1} \left\langle \sum_j \delta[\bar{r}_j - \bar{r}(t) - \bar{r}] \right\rangle \quad (4.2)$$

where $\bar{r}(t)$ is the position of the hydrogen ring polymer at time it in the imaginary time interval between 0 and $i\beta\hbar$, $\bar{r}_j$ is the position of the j th hydrogen solvent particle and ρ_s is the density of solvent. The brackets denote the equilibrium ensemble average. The function $\bar{r}(t)$ for $0 \leq t \leq \beta\hbar$ is the hydrogen ring polymer path. The paths are periodic with period $\beta\hbar$, and thus the hydrogen is viewed geometrically as a ring polymer. In the adiabatic approximation, the path of the classical solvent particles are taken as points.

We use the theory^{7,8} developed by Chandler et. al. to calculate $\omega_p(r, t - t')$. This approach uses Feynman's polaron approximation in which an optimum harmonic reference functional is identified, and the behavior of $\omega_p(r, t - t')$ is determined self-consistently by that reference. Since harmonic functionals coincide with Gaussian statistics, all the predictions we make concerning the hydrogen polymer response are contained in the second moment

$$\mathcal{R}^2(t - t') = \langle |\bar{r}(t) - \bar{r}(t')|^2 \rangle \quad (4.3)$$

The quantity $\mathcal{R}(t - t')$ is the mean square displacement between two points on the hydrogen polymer path separated by a time increment $0 \leq t \leq \beta\hbar$. The characteristic size or breadth of the quantum particle (or polymer ring) is

$$\mathcal{R} = \mathcal{R}(\beta\hbar/2) \quad (4.4)$$

This distance represents a correlation length since the hydrogen polymer's linear response at $\vec{r}'$ due to a localized disturbance of the ring at $\vec{r}$ is proportional to $\omega_p(\vec{r}, t - t')$. The maximum range of this response is roughly $\mathfrak{R}$.

The primary physical phenomenon which was supposed to be addressed in this theory is the process of localization or self-trapping of the hydrogen polymer ring due to the presence of the classical hydrogen solvent. At low solvent densities, the hydrogen polymer is fairly extended, fluctuating with nearly the free particle Gaussian statistics where the radius of gyration is given exactly by

$$R_{\text{free}}^2 = \frac{\lambda^2}{4} \left(1 - \frac{1}{p^2} \right) \quad (4.5)$$

where p is the number of beads on the hydrogen polymer ring. The overall size of the extended hydrogen molecule is therefore approximately λ . At high densities we observe that the radius of gyration is not significantly reduced and therefore there is not an appreciable amount of self-trapping.

We calculate the solvation potential by solving the PRISM equations, which can be written in Fourier space as

$$\hat{h}_{ps}(\mathbf{k}) = \hat{\omega}_p(\mathbf{k}) \hat{C}_{ps}(\mathbf{k}) \hat{S}_{ss}(\mathbf{k}) \quad (4.6)$$

where $h_{ps}(r)=g_{ps}(r)-1$, $C_{ps}(r)$ is the corresponding direct correlation function, and $\hat{S}_{ss}(k)$ is the structure factor for the classical hydrogen solvent bath. The PRISM equation is solved with the Percus-Yevick closure relation:

$$C_{ps}(r) = g_{ps}(r) \{1 - \exp[\beta v(r)]\} \quad (4.7)$$

The Silvera-Goldman potential Eq. (3.1) is used for the interaction potential between a bead on the polymer ring and a classical H_2 particle.

With the direct correlation function determined through the PRISM theory, we approximated^{7,9} the medium-induced potential $v_{pp}[r, \omega(r)]$ between beads of the polymer ring using either of the two equations below

$$\hat{\omega}[k, \hat{\omega}(k)] = -\ln \{1 + \rho_s \hat{C}_{ps}(k) \hat{S}_{ss}(k) \hat{C}_{ps}(k)\} \quad (4.8)$$

or

$$\hat{\omega}[k, \hat{\omega}(k)] = -\rho_s \hat{C}_{ps}(k) \hat{S}_{ss}(k) \hat{C}_{ps}(k) \quad (4.9)$$

The PRISM equations were solved with the Percus-Yevick closure self-consistently with either Eq. (4.8) or (4.9) for the solvation potential. The $\mathcal{R}(\tau)$ correlation functions that result from this calculational procedure are shown in figure 6.

Figure 6 – Correlation function versus imaginary time for several densities at 45 °K.

It can be seen from these figures that the paths $\mathcal{R}(\tau)$ do not change very significantly as the density is increased from zero. Thus there is not a significant amount of self-trapping or localization in these H_2 liquids at these temperatures.

Another measure of the degree to which the H_2 molecule is delocalized in the bulk liquid state is given by the radius of gyration. Results from the PRISM calculations are shown in figure 7 and 8 along with the corresponding simulation results. It can be seen from these figures that the degree of localization of the H_2 molecule does not change dramatically over the range of temperatures and densities studied. It is also of interest to examine the intermolecular pair correlation function $g(r)$ between a classical and quantum H_2 molecule shown in figure 9.

Figure 7 – Mean square radius of gyration of H_2 at 45°K. Points are from the simulation in Table 1. Upper line uses the medium induced potential of Eq. (4.9); the lower curve is from Eq. (4.8)

Figure 8 – Mean square radius of gyration versus temperature. Points and lines are as in figure 7.

Figure 9 – Pair correlation function between a classical and quantum H_2 molecule at 35°K and 50 mol/l. calculated from PRISM theory. The dotted curve is for a free particle at zero density and the dashed/dot curve is in the dense liquid.

Very little difference can be seen in the correlation function between a free particle and zero density and the fully dense liquid. This again suggests that hydrogen molecules undergo very little delocalization as a result of the surrounding liquid molecules. This is in sharp contrast to results found previously by Chandler and coworkers^{7,8} for electrons in a classical liquid. The differences can be attributed to the fact that electrons are much lighter, and hence have significantly larger quantum effects, than hydrogen nuclei.

V. Hydrogen Adsorption on Surfaces

We now turn our attention to hydrogen molecules adsorbed on various surfaces. This is an important problem to Sandia because of the importance of hydrogen storage and embrittlement in metals. One very basic calculation we performed^{10,11} involved the adsorption on graphite, comparing it directly with experiment. We point out that there

does not exist a large body of experimental data for hydrogenic adsorption. This can no doubt be attributed to the difficulty of adsorption experiments at low temperature and low pressure. A notable exception is the adsorption work performed by Liu at the University of Washington (Liu, 1993). These measurements focused on HD adsorbed on graphite. We have used their work to test our methods and potentials. As an example, we show an adsorption isotherm at a temperature of 13.28K in figure 10.

Figure 10. Adsorption isotherm for HD on graphite at 13.28 K. The open circles are the experimental data of Y. M. Liu [Ph.D. Thesis, University of Washington, Seattle, 1993] and the filled circles are the results of path integral simulations.

The path integral simulation data can be seen to be in good overall qualitative agreement with the experimental results. Both simulation and experiment exhibit a transition in the adsorption near a pressure of about 0.13 Torr. The transition appears to be first order in both cases. From the simulation it is evident that this transition coincides with the completion of a second layer of HD on the graphite surface. The size of the jump in adsorption at this pressure is also well captured by the simulation. However, overall the simulation prediction for the adsorption is about 10-20% too low. It is possible that

some the experimental adsorption is due to pore spaces, which are not captured by the simulation.

We have also performed a studies of hydrogen adsorption in a variety of porous adsorbents. A particular goal of these simulations was the issue of quantum effects on the capillary condensation transition. This was investigated by directly comparing a classical simulation with a path integral simulation for the same system, interacting with the identical intermolecular potential. The porous material used was a graphite slit pore with a width of 3.5 molecular diameters.

The simulations show that both classical and quantum hydrogen undergo capillary condensation (see Figure 11). However, the transition for quantum hydrogen is significantly delayed to higher pressures.

Figure 11. Adsorption isotherms for classical (open circles) and quantum (filled circles) hydrogen in a graphitic slit pore of width 3.5 molecular diameters. The reduced temperature is 0.606 with respect to the critical temperature. This corresponds to 20 K for classical hydrogen and 15.2K for quantum hydrogen

There exists a range of pressures where classical hydrogen is a confined liquid and quantum hydrogen is a confined gas, the quantum behavior leads to suppression of

capillary condensation. A further examination reveals that it is the larger average size of quantum hydrogen that shifts the transition to larger pressures. The quantum suppression of capillary condensation is diminished as one moves to larger pore sizes.

We have also performed path integral simulations to explore the possibilities of quantum sieving, i.e. a separation of hydrogen isotopes solely due to their quantum nature. Preliminary results indicate that with the right size (small) pore a situation can indeed arise where the lighter isotope, due to its larger quantum fluctuations can not enter pores.

The newly developed single walled carbon nanotubes (SWNT) have attracted much recent attention as possible candidates for highly efficient hydrogen storage. To study the adsorption potential of SWNTs we have recently embarked on a comprehensive study of these systems, and comparing them with graphite slits. In particular, we have focused on the so-called usable capacity ratios, defined as the ratio of usable hydrogen stored by physisorption and compression. We find that, contrary to initial suggestions nanotubes, commonly produced in crystalline bundles of SWNTs, are not especially good media for hydrogen storage. Indeed, we find that the capacity ratios for the (9,9) and (18,18) tubes are smaller than any of the graphite slit geometries. (See Figure 12). However, the simulations indicate that there is potential for improvement of hydrogen storage in SWNTs if the lattice spacing of an array of SWNTs is optimized for adsorption, exploiting adsorption onto the outer surface of the tubules.

Figure 12. Usable capacity ratios for SWNT arrays and graphitic slit pores at 298 K. The filled circles are for the (9,9) tube, the filled triangles are for the (18,18) tube, and the open triangles, circles, and squares are for slit pores of 2, 3, and 6.67 molecular diameters, respectively.

A demonstration of this effect is presented in figure 13, which displays the complete radial density profile (internal and external) for an isolated tube at 50K and 50 atm. The external adsorption constitutes a significant fraction of the total amount adsorbed.

Figure 13. The density profile of hydrogen adsorbed on the internal and external surfaces of an isolated SWNT at 77 K and 50 atmospheres. The center of the tube is located at $r^* = 0$.

VI. Simulation Strategies

The simulation of a ring polymer might proceed like that of any other polymer, not taking note of the special type of interactions. That is, one can use either conventional parallel Monte Carlo (MC) or conventional Molecular Dynamics (MD). To parallelize a code one would choose from the familiar strategies including those based on spatial decomposition and force decomposition. There are two aspects that need special consideration: One is the existence of stiff springs. The second is the special interactions between beads on different polymers. We will start the discussion with the springs.

The Gaussian spring potential that connects nearest neighbor beads on the same ring tend to be much stiffer than the Lennard-Jones or Goldman-Silveira potential that acts between beads on different rings. In addition, the stiffness increases when the number of beads increases and also when the temperature decreases. The presence of slowly and fast varying interactions is common to simulations of molecules with internal degrees of freedom. Traditionally there was only one way to deal with this, small timesteps Δt in MD or small trial moves in MC. However, in the early 1990's Tuckerman¹² et al. have suggested a novel systematic approach based on the Liouville formulation of classical mechanics. These authors showed how to systematically derive time reversible and area-preserving MD algorithms, using a Trotter expansion of the time-evolution operator. The velocity-Verlet algorithm is the best known example of this class. One application is the so-called Multi Time Stepping (MTS) algorithm that is particularly suited to MD for molecules with stiff bonds. In essence MTS allows one to mix small and large time steps and hence gain in computing efficiency.

An alternative approach that is also made possible by the time reversible area-preserving MD algorithms is Hybrid Monte Carlo. The key insight is to use MD to generate a collective trial move for MC. The basic idea here is to choose a Δt that is very large such that in a one or a few time steps one generates what constitutes a good collective MC trial move. The collective aspect implies that rather than displacing a single particle in a move we move all N particles in this scheme. Of course, the size of such a Δt will be too large to conserve energy, and a ΔE results. Thanks to the time-reversible area-preserving properties of the MD algorithm one can use the generated configuration as a trial move and decide, with a Metropolis algorithm (with ΔE as input), whether to reject or accept the configuration. In this scheme the particle velocities need to be randomized at the beginning of the MD phase. Since the diffusion improves if some equilibration is allowed in practice the MD phase typically consists of several time steps. Hybrid MC can be advantageous as the large Δt allows one to sample phase space more quickly than would be the case with energy conserving values for Δt . The hybrid MC suffers from one single drawback that is shared with all MC approaches based on collective moves however. Since ΔE grows as $N^{1/2}$ the acceptance probability decreases as the system gets large, thus ultimately offsetting the gains of a large Δt .

A special feature of Feynman's isomorphism involves the interaction of beads between different rings. Each bead interacts with only *one* bead on a different ring, as the interaction only exists between beads in the same 'time slice'. To be specific, if each ring consists of p beads labeled 1 to p , then bead 1 on rings 1, 2, ... only interacts with all other beads 1 that are part of the other rings, and similarly bead p on rings 1, 2, ...

Figure 14 – A schematic representation of the simulation procedure

only interacts with all other beads p that belong to other rings. One way to illustrate this is shown in figure 14. This figure illustrates a 2D simulation of 8 quantum particles (we leave the illustration of a 3D system as an exercise to the interested reader). Each quantum particle is represented by a ring of 6 beads. The rings have been drawn vertically for the purpose of clarity. Each bead is connected via a spring to its two nearest neighbors (the springs at the bottom of the figure, in slice 6, connect to the beads at the top of the figure, slice 1). Note that each time slice k , consists of all the k^{th} beads of each ring. Two such slices have been drawn in figure 14. *Within* a given time slice the simulation problem is identical to that of any regular simple atomic fluid – the

interactions within a slice are simple short range, non-bonded fluid interactions (here, LJ or Goldman-Silveira). Indeed, figure 14 makes it clear that without the springs the simulation problem would be that of 6 independent simulations of 8 particles each. The springs provide the coupling between two consecutive time slices, and it is their presence that makes the 6 simulations in the time slices interdependent. But notice that the coupling is of an extremely simple variety, as it only acts between two particles at a time.

Clearly, the complexity of the quantum simulation resides largely within the time slices where it is identical to that of a simple atomic fluid. The coupling between the slices is trivial in comparison. Not only is the force law simple, it always occurs between the same beads and the same number of beads (i.e. each bead has exactly two nearest neighbors) and thus does not require any updates in book keeping as the simulation proceeds. In addition, in practice the typical number of beads, p , is limited to a value between 10 and 100. We conclude therefore that the parallelization aspects are not significantly more complicated than those of traditional classical simulation algorithms.

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