Restricted Path-Integral Molecular Dynamics for Simulating the Correlated Electron Plasma in Warm Dense Matter

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Outline

- Path-Integral Formulation
- Computational Implementation
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Path-Integral Formulation

Partition function of quantum system

$$Z = \int dR_1 \rho(R_1, R_1; \beta) = \int \prod_{n=1}^{P} dR_n \prod_{n=1}^{P} {}^{*}\rho(R_n, R_{n+1}; \epsilon)$$

* Means closure condition

$$R_{P+1} = R_1$$

For fermions the density matrix can be negative
Restricted path Integral for Fermion systems

$$Z = \int \prod_{n=1}^{P} dR_n \prod_{n=1}^{P} {}^{*}\rho(R_n, R_{n+1}; \epsilon)\, \theta^{+} = \int \prod_{n=1}^{P} dR_n \exp[-\beta V_{\text{eff}}(R_1, \ldots, R_P)]$$

θ^{+} restricts paths to positives density matrices

Effective "classical potential"

$$V_{\text{eff}} = \begin{cases} -\frac{1}{\beta} \sum_{n=1}^{P} {}^{*} \ln \rho(R_n, R_{n+1}, \epsilon) & \text{if } \theta^{+} = 1 \\ \infty & \text{if } \theta^{+} = 0 \end{cases}$$

Path-Integral Formulation

$$V_{\text{eff}}^{\text{exch}}(R_1,\ldots,R_P)=\sum_{i=1}^{P}\sum_{k>l}^{N_{\text{el}}}\sum_{l=1}^{N_{\text{el}}-1}\frac{(-e)(-e/P)}{4\pi\epsilon_0|r_i^{(k)}-r_i^{(l)}|}$$

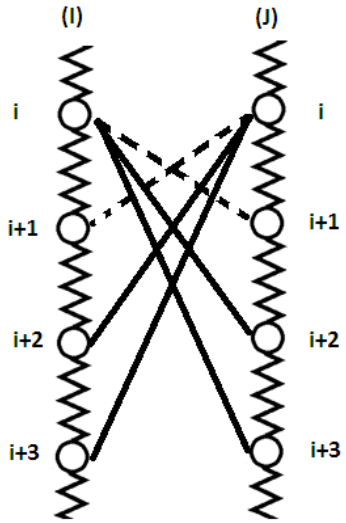
Electron-electron Coulomb potential

$$+\sum_{k=1}^{N_{\text{el}}}\sum_{i=1}^{P} * \frac{m_e P}{2\hbar^2\beta^2}(r_i^{(k)}-r_{i+1}^{(k)})^2$$

Non-exchanging quantum particles represented as harmonic chains of P beads

$$-\frac{1}{\beta}\sum_{s=\uparrow}^{\downarrow}\frac{\sum_{i=1}^{P}\sum_{j=1}^{P}\ln\det[E_{ij}]_s\,\theta_{ijs}^{+}}{\sum_{i=1}^{P}\sum_{j=1}^{P}\theta_{ijs}^{+}}$$

Non-local exchange term between isospin (s) particles



where $E_{n,n+1}^{ij}=A_{n,n+1}^{ij}/A_{n,n+1}^{ij}$

$$A_{n,n+1}^{ij}=\exp\left[-\beta\frac{m}{2\beta\epsilon\hbar^2}(r_n^{(i)}-r_{n+1}^{(j)})^2\right]$$

Exchange=Cross linking of harmonic necklaces (I) and (J)

Computational Implementation

Classical effective Hamiltonian for N Fermions (k) in the potential field of N_{ions} for molecular dynamics sampling

$$H=\sum_{k=1}^{N_{el}}\sum_{i=1}^{P}\frac{1}{2}m^{*}(\dot{r}_i^{(k)})^2+\sum_{I=1}^{N_{ion}}\frac{1}{2}M_I\dot{R}_I^2$$

Classical kinetic energy of beads (artificial mass m*) and ions

$$+\sum_{I>J}^{N_{ion}}\sum_{I=1}^{N_{ion}-1}\Phi_{IJ}(r_{IJ})+\sum_{i=1}^{P}\sum_{k>1}^{N_{el}}\sum_{l=1}^{N_{el}-1}\frac{(-e)(-e/P)}{4\pi\epsilon_0|r_i^{(k)}-r_i^{(l)}|}$$

Ion-Ion and electron-electron potential interactions

$$+\sum_{i=1}^{P}\sum_{k=1}^{N_{el}}\sum_{I=1}^{N_{ion}}\frac{V_{pseudo}(R_I-r_i^{(k)})}{P}$$

Electron-ion pseudo-potential

$$+\sum_{k=1}^{N_{el}}\sum_{i=1}^{P}*\frac{m_eP}{2\hbar^2\beta^2}(r_i^{(k)}-r_{i+1}^{(k)})^2$$

Quantum particle necklaces

Exchange

$$-\frac{1}{\beta}\sum_{s=\uparrow}^{\downarrow}\frac{\sum_{i=1}^{P}\sum_{j=1}^{P}\ln\det[E_{ij}]_s\theta_{ijs}^{+}}{\sum_{i=1}^{P}\sum_{j=1}^{P}\theta_{ijs}^{+}}.$$

The matrix $[E_{n,m}]$ for each spin should be a $27N_{\uparrow,\downarrow}\times 27N_{\uparrow,\downarrow}$ matrix. In order to make the calculation more tractable, we make the numerical approximation $\det[E_{n,m}]\approx C\det[F_{n,m}]$, where $[F_{n,m}]$ is an $N_{\uparrow,\downarrow}\times N_{\uparrow,\downarrow}$ matrix that off-diagonal elements give the maximum contribution of pair exchange to the determinant among the possible combinations of exchange between the electrons in the simulation cell and the electrons in all periodic cells.

Computational Implementation

- Classical molecular dynamics (MD) algorithm
- Nose-Hoover chain of 5 thermostats for each necklace
- Periodic boundary conditions (special attention paid to necklace integrity and exchange)
- Unpolarized electron plasma: 54 electrons (27 spin up and 27 spin down)
- Ewald summation method for long-range Coulomb interaction
- Exchange potential scales as $P^2 N_{\uparrow,\downarrow}^3$
- Exchange potential (forces) part of the algorithm parallelizable over P beads

Results

Energies for Low T Low density Plasma

Convergence of algorithm

Validation of algorithm

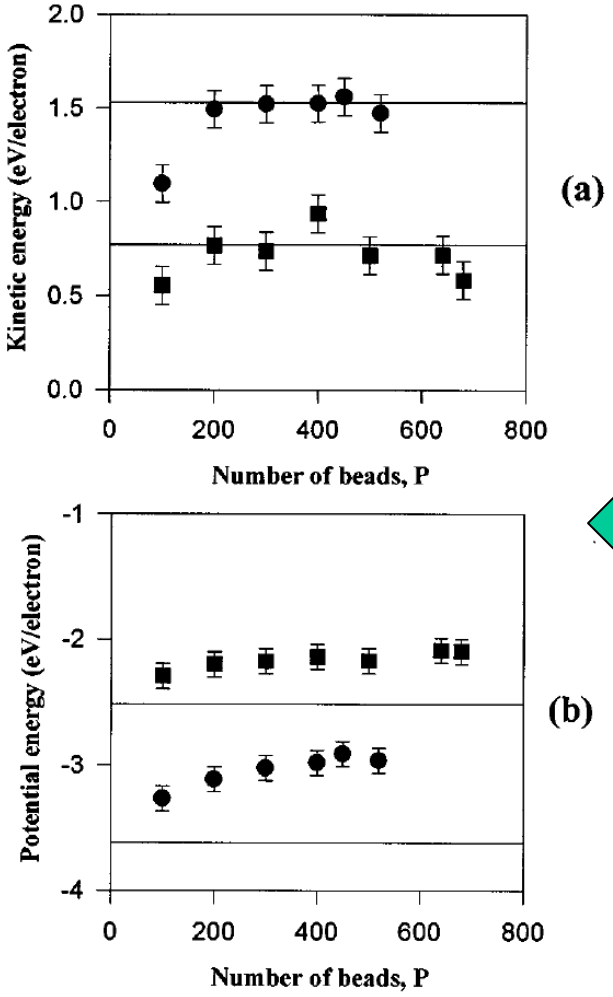


FIG. 1. (a) Kinetic energy and (b) potential energy as functions of the number of beads in the necklace representation of quantum particles. The circles and squares refer to the high-density ($r_s = 5a_0$, $T = 1800$ K) and medium-density ($r_s = 7.5a_0$, $T = 700$ K) electron plasmas, respectively.

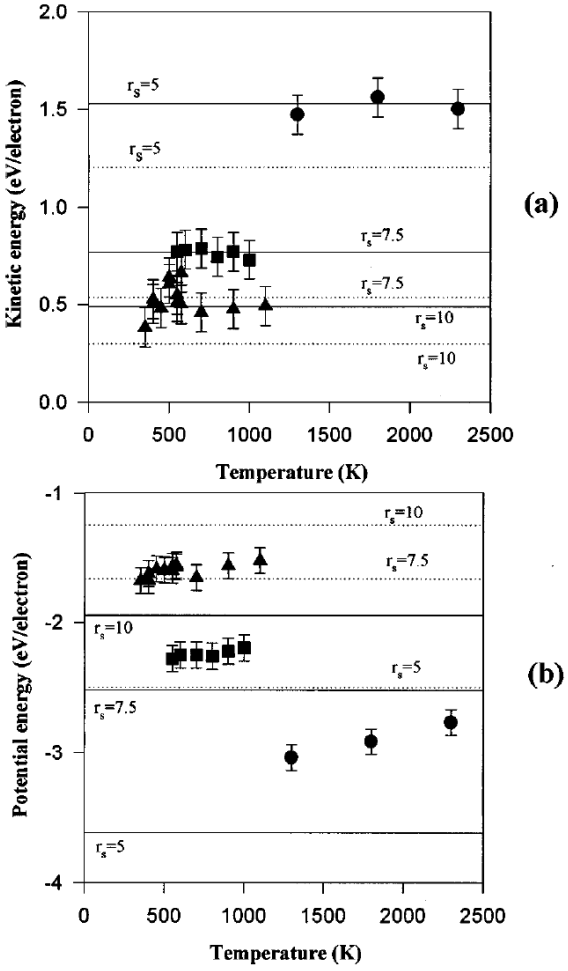
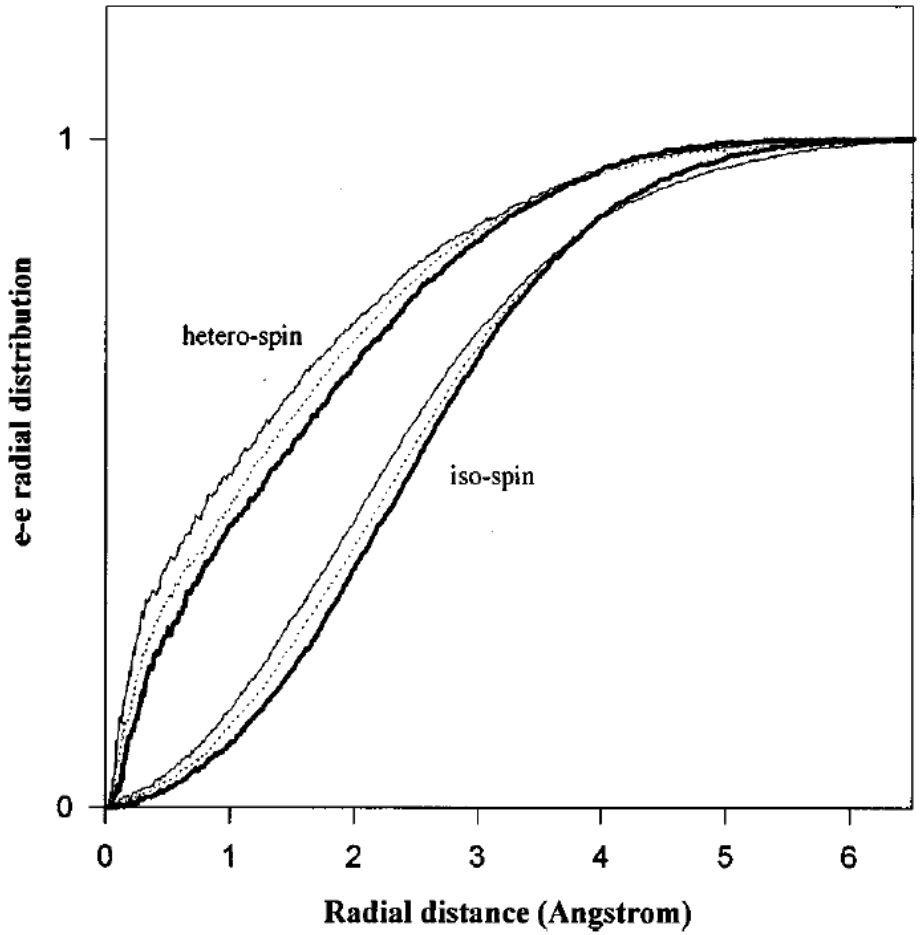


FIG. 2. (a) Kinetic energy and (b) potential energy as functions of temperature. The electron plasmas with $r_s = 5a_0$, $7.5a_0$, and $10a_0$ are denoted by circles, squares, and triangles, respectively. The horizontal lines correspond to the correlated energies of Ceperley (Ref. 16). The dotted lines indicate the Hartree-Fock energies.

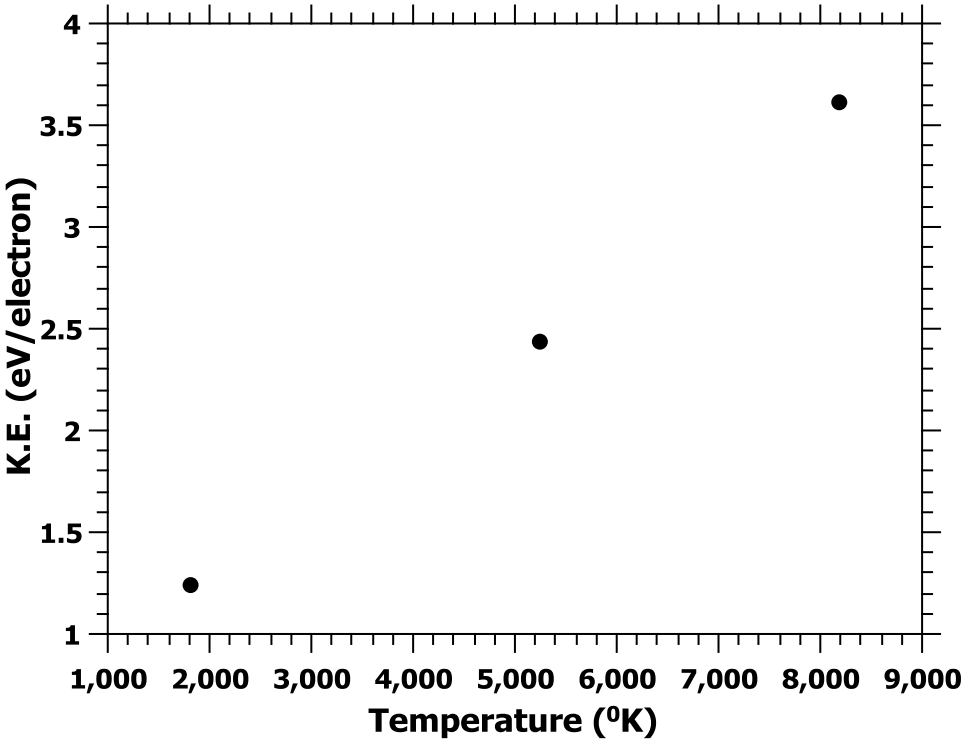
Results



Effectiveness of "Classical" exchange potential at creating exchange-correlation hole

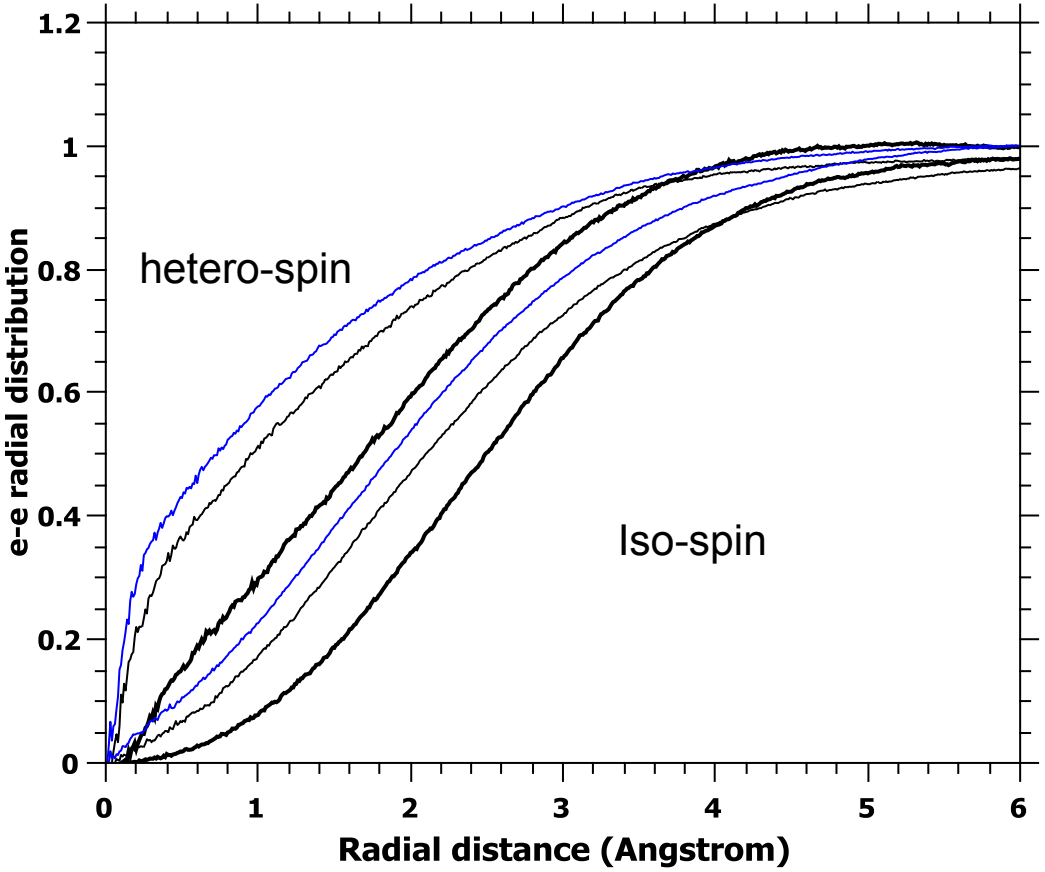
FIG. 3. Isospin and heterospin electron-electron pair distributions for the high-density electron plasma at $T = 1300$ K (thick solid line), $T = 1800$ K (dotted line), and $T = 2300$ K (thin solid line).

Results



Electron plasmas with rs=5a0.

Results



Iso-spin and heterospin electron-electron pair distributions for the high density electron plasma at T = 1800 K (thick solid line), T = 5000 K (dotted line), and T=8000 K (thin blue line)

Conclusions

- PIMD has successfully reproduced the known results of electron plasmas for the low temperature and low densities.
- Extended the PIMD calculations for determination of electron plasma properties at medium temperature and densities.
- PIMD is an appropriate tool for exploring WDM and parallelization of the algorithm will lead to substantial improvements in computational performance of the procedure.

Future Work

- Future work will involve calculations at temperatures [10kK, 100kK] and Seitz radii 2, 1, 0.5.
- The PIMD method has the ability to include ions, so it will be used to compare other calculations (e.g., Lithium) being done by the WDM ofDFT group at UF.
- Another interesting problem to study will be immersing of ionic system inside the electron plasma (e.g., H_2 in an electron plasma).

Acknowledgment

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