The Uniform Electron Gas at Warm Dense Matter Conditions


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Introduction: warm dense matter

Warm dense matter (WDM):

- Nearly classical ions
- Degenerate non-ideal electrons
- Coupling parameter:
  \[ r_s = \frac{\bar{T}}{a_B} \sim 0.1 \ldots 10 \]

- Degeneracy parameter:
  \[ \theta = \frac{k_B T}{E_F} \sim 0.1 \ldots 10 \]

- Temperature, degeneracy and coupling effects equally important
  → No small parameters
  → Perturbation theory and ground-state approaches (DFT etc.) fail

Improved *ab initio* simulations needed to capture all effects in WDM
The uniform electron gas - Coulomb interacting electrons in a uniform positive background

**Ground state:**
- Model description of metals
- **Input for density functional theory (DFT)**
- Accurate parametrization of XC-energy\(^1\) for all \(r_s\) from ground state Monte Carlo data\(^2\)
  → DFT simulations of real materials

**Warm dense matter:**
- Ground state DFT not sufficient\(^3\)
  → **Thermal DFT**\(^4\)
  → Requires finite-\(T\) XC-functional\(^3\)
    (XC free energy \(f_{xc}\))
- Finite-\(T\) XC-functional directly incorporated into
  - **EOS models** of astrophysical objects\(^5\)
  - **approximations in QHD**\(^6\)

Reliability of these approaches crucially depends on accurate parametrization of \(f_{xc}(r_s, \theta)\)

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3. V. Karasiev et al., PRE 93, 063207 (2016)  
Many parametrizations for $f_{xc}$ based on different approximate approaches:

- Semi-analytical approaches by Ebeling\(^1\)
- Dielectric methods, e.g. Singwi-Tosi-Land-Sjölander\(^2\) (STLS) and Vashista-Singwi\(^3\) (VS)
- Quantum-classical mappings, e.g. Perrot and Dharma-wardana\(^4\) (PDW)
- **Most recent**: Fit by Karasiev\(^5\) *et al.* (KSDT) to Restricted Path Integral Monte Carlo (RPIMC) data\(^6\)

**But**: RPIMC invokes *fixed node approximation* → induces *uncontrolled systematic errors*\(^7\)

**Accuracy of existing parametrizations for $f_{xc}(r_s, \theta)$ unclear**

*Ab initio* description of the warm dense UEG highly needed

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5. V.V. Karasiev *et al.*, PRL 112, (2014)
Path integral Monte Carlo (PIMC) simulation of the warm dense UEG

- Standard PIMC in warm dense regime severely hampered by **fermion sign problem**:
  - First results\(^1\) by E. Brown, D. Ceperley *et al.* (2013) based on **fixed node approximation** (RPIMC)
  - Induces **systematic errors** of unknown magnitude
  - RPIMC limited to \( r_s \gtrsim 1 \)

**Our approach:**
Avoid fermion sign problem by combining two novel **exact** and complementary QMC methods:

1. **Configuration PIMC (CPIMC)**\(^2,3\)
   - Excels at high density \( r_s \lesssim 1 \) and strong degeneracy
2. **Permutation blocking PIMC (PB-PIMC)**\(^4,5\)
   - Extends standard PIMC towards stronger degeneracy

**Exact ab initio simulations over broad range of parameters**

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Results I: CPIMC for $N = 33$ spin-polarized electrons

Exchange-correlation energy $E_{xc} = E - E_0$ ($E_0$ : ideal energy)


RPIMC carries systematic errors exceeding 10%
Results II: Combination of CPIMC and PB-PIMC

- RPIMC limited to $r_s \geq 1$
- CPIMC excels at high density
- PB-PIMC applicable at $\theta \gtrsim 0.5$

Combination\(^1\) yields exact results over entire density range down to $\theta \sim 0.5$.

- Also applies to the unpolarized UEG\(^2\)
- Our results confirmed by recent DMQMC simulations\(^3\)

**UEG well understood\(^4\) for finite $N$**

How to extend the simulations to the thermodynamic limit ($N \to \infty$) ???

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\(^1\) S. Groth et al., Phys. Rev. B 93, 085102 (2016)
Results III: Extension to thermodynamic limit

- QMC results are afflicted with finite-size error $\Delta V(N)$ (exceeding 20%)
- Extrapolation and previous finite-size\(^2\) corrections are unreliable
- **Solution:** Combine QMC data for $S(k)$ with long-range behavior from RPA, STLS [exact for $S(k \to 0)$]

**Improve finite-size correction for all WDM parameters!**

\[ \nu = \frac{V_N}{N} + \Delta V(N) \]
Results IV: Extension to ground state

- With our two novel quantum Monte-Carlo (QMC) methods\(^1\)\(^-\)\(^4\) and improved FSC\(^5\) we obtained the first unbiased QMC data\(^5\) for the potential energy of the UEG over the entire \(r_s-\theta\)-plane for \(\theta \geq 0.5\) (restriction due to fermion sign problem).

- For \(\theta = 0\) use exact ground state QMC data\(^6\) \(v_0\)

- For \(0 < \theta < 0.25\) add (small) STLS\(^7\) temperature-correction to \(v_0\)

\[
\nu(\theta) = v_0 + \left[ \nu^{\text{STLS}}(\theta) - \nu^{\text{STLS}}(0) \right]
\]

→ Highly accurate (~ 0.3%) data set for \(\nu(\theta, r_s)\) over entire WDM regime

- Exchange-correlation free energy \(f_{xc}\) linked to potential energy via

\[
2f_{xc}(r_s, \theta) + r_s \frac{\partial f_{xc}(r_s, \theta)}{\partial r_s} \bigg|_{\theta} = \nu(r_s, \theta)
\]

- Use suitable parametrization for \(f_{xc}\) and fit l.h.s. to r.h.s.

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\(^5\) T. Dornheim \textit{et al.}, PRL \textbf{117}, 156403 (2016)  
Results V: Parametrization of $f_{xc}(r_s, \theta)$


**Construct finite-$T$ XC-functional:**

- Temperature-corrected ground state data smoothly connects to exact finite-$T$ QMC data (over entire WDM regime)
  → Smooth fit through all data points for $\nu(r_s, \theta)$

→ Obtain highly accurate ($\sim 0.3\%$) parametrization for $f_{xc}$

**Comparison to other parametrizations reveals deviations of $\sim 5-12\%$ (depending on $r_s$ and $\theta$)**
Results VI: Ab initio description of spin-polarization effects


- DFT in local spin-density approximation requires $f_{xc}(r_s, \theta)$ at arbitrary $\xi = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$
- Extend parametrization $f_{xc}(r_s, \theta) \rightarrow f_{xc}(r_s, \theta, \xi)$
- Extensive new QMC data for $\xi = 0, 1/3, 0.6, \text{and } 1$

→ First *ab initio* $\xi$-dependency

No previous parametrization captures correct spin-dependency of $f_{xc}$
Summary:

- QMC at finite-\( T \) severely hampered by \textit{fermion sign problem} (FSP)
  → Common solution: \textit{fixed node approximation} (RPIMC)\(^1\) → systematic errors exceed 10\%\(^2\)
- \textbf{Our approach:} circumvent FSP by combining \textbf{two novel exact QMC methods}\(^3,4\)
- Presented \textbf{improved finite-size correction}\(^5\) → Extrapolate finite-\( N \) QMC data to TD limit
  
  \begin{center}
  \textbf{First exact data of the warm dense UEG down to} \( \theta = 0.5 \)\(^5\)
  \end{center}

- Combined \textbf{ground state QMC data}\(^6\) + \textbf{STLS temperature-correction} for \( \theta \leq 0.25 \)

  \begin{center}
  \textbf{Accurate (\( \sim 0.3\% \)) and consistent parametrization}\(^7\) of \( f_{xc} \) across entire \( r_s-\theta-\xi \)-space for the UEG at WDM conditions (\( r_s \lesssim 20, \theta \lesssim 8 \))
  \end{center}

- \textbf{First benchmarks of previous parametrizations}\(^7\)
  - Systematic errors of 5 – 12\% in WDM regime
  - Unsatisfactory description of spin-dependency


Concluding remarks:

- Use our new $f_{xc}$-functional as input for
  - DFT calculations
  - Quantum hydrodynamics
  - Equation of state models of astrophysical objects
- Functional available online (C++, Fortran, Python) at https://github.com/agbonitz/xc_functional
- Implemented in libxc4.0.4: LDA_T_GDSMFB

Outlook:

- *inhomogeneous* UEG
  - Access to static local field correction
- *ab initio* results for imaginary-time correlation functions
  - Reconstruction of dynamic structure factor $S(q, \omega)^1$

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1. T. Dornheim, PhD thesis, Kiel University 2018
Bonitz group homepage: [http://www.theo-physik.uni-kiel.de/bonitz/](http://www.theo-physik.uni-kiel.de/bonitz/)

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