Quantum clusters: finite temperature variational quantum hydrodynamics

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Problem: how to use Bohm-inspired ideas?

• We’ve heard plenty about attempts to use Bohm trajectories for doing quantum dynamical calculations.

• Mostly model, 1D (or few D) problems that can be approached more efficiently using “standard” methods

\[ Q(x) \propto \frac{1}{\psi(x)} \psi''(x) \]

• PROBLEM: Quantum potential becomes singular.

• WANTED: a problem that is difficult to solve using “traditional” methods and one in which “Bohm-inspired” methods offer a solution in an efficient way.

• WANTED: flexibility to use the approach for a wide range of problems.

• Karl Freed (U. Chicago) “Too much rigor makes for rigor mortis.”
#1: Let’s forget about real-time dynamics

- For stationary states. Do not have to worry about the “node problem”

\[ E\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \]

\[ E = -\frac{\hbar^2}{2m \psi} \nabla^2 \psi + V \]

\[ Q(x) = -\frac{\hbar^2}{2m \psi} \nabla^2 \psi = E - V(x) \]

\[ Q(x) = E - V(x) \]

no “node problem” for all stationary states!!

no singularities
Bohm/Monte Carlo idea.

  - Sample the quantum density using Monte Carlo.
  - Use “maximal entropy” method to get $n(x)$
  - Use $n(x)$ to obtain quantum potential: $Q[n] = \frac{-\hbar^2}{2m} \frac{1}{\sqrt{n}} \nabla^2 \sqrt{n}$
  - Move sample points along conjugate gradient of $E[n] = Q[n] + V[n]$ so that $\partial E = 0$
- At true ground state: sample points are stationary!
- Thermal effects can be included by performing calculations in a statistical ensemble (Mermin).
Mixture model \[ n(r) = \sum_{m}^{M} p(r, \{c_m\}) \]

\[ p(r,\{c_m\}) = \text{prob. that a randomly chosen member of ensemble will have configuration } r \text{ and is a variant of the } m\text{th approximate designated by } \{c_m\} \text{ (Joint probability)} \]

\[ p(r,\{c_m\}) = p(\{c_m\}) p(r \mid \{c_m\}) = n(r)p(\{c_m\} \mid r) \]

\[ p(r \mid \{c_m\}) = \text{prob. that a randomly chosen variant of } \{c_m\} \text{ has config. } r \]

\[ p(\{c_m\} \mid r) = \text{prob. that } r \text{ is a variant of } \{c_m\} \]

Bayes’ Equation:

\[ p(c_m \mid r_n) = \frac{p(\{c_m\}) p(r \mid \{c_m\})}{\sum_{m} p(\{c_m\}) p(r_n \mid \{c_m\})} \]

Note: Can choose approximates \( p(r\{c_m\}) \) in a variety of ways. Easiest = gaussian with sparse covariance. (e.g. factored between different d.o.f.)
More exact: choose covariance perhaps correlating multiple atoms, d.o.f, etc.
Estimating density using n-Gaussian approximates

FIG. 2: This figure illustrates the EM algorithm for the data pictured in Fig. 1 using 16 separable Gaussian clusters. The contours reflect the approximated probability density during the course of the EM fitting routine. The black dots correspond to the average position of the Gaussian cluster, and the solid black ellipses represents the Gaussian half-width contours.

Relaxation on a model Potential Surface (Mel)

FIG 7: Plots ras and rbs show the relaxation of a Gaussian wave packet in an anharmonic potential well for both the separable and fully covariant models respectively. The gray contours reflect the potential energy curves for a model of CH$_3$Ix. The shaded contours indicate the shape of the approximated density after r1s zv r2z v z v and r3z v z v Verlet time steps respectively. The solid curves represent the half-width contours of the Gaussian clusters. Plot rcs shows the numerically accurate DVR ground state and the associated grid of quadrature points. Plot rds shows the energy of the estimated density as a function of time steps. The dotted and solid data corresponds to the separable and nonseparable models respectively, while the dashed horizontal line represents the DVR energy.

#2: Ask: When are QM effects important?

- DeBoer Ratio: ratio of de Broglie wavelength to range of potential

\[ \Lambda = \frac{\lambda(T^*)}{\sigma} = \frac{\hbar}{\sigma \sqrt{m\epsilon}} \]

\[ T^* = \frac{\epsilon}{\hbar} \quad \text{effective T in terms of well-depth} \]

Classical limit \( \Lambda = 0 \)

“Strongly QM” \( \Lambda > 0.3 \) (Liq. He)

Liquid Ne: \( \Lambda_{Ne} > 0.1 \)

**Physical Question:** Are there appreciable quantum contributions to structure/thermodynamics of clusters?
System: Quantum rare-gas clusters

Energy density functional:  
\[ E[n(r_1, \ldots, r_N)] = T[n] + V[n] \]
T = 0K theory

\[
H = - \sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i \neq j} V(ij),
\]

Energy is a functional of the configurational density \( n(r_1, ..., r_N) \)

\[
E[n(r_1, ..., r_N)] = T[n] + V[n]
\]

Ground state: \( \frac{\delta E[n]}{\delta n} = 0 \)

\[
\Psi(r) = \sqrt{n(r)} e^{i\phi}
\]

\( \phi(r) = \text{const.} \)
Density factorization (mean field approx)

Configurational Density \( n(12345) \)
q.m. prob. for finding system in a given atomic configuration

Approx: full config. density as a sum over “statistical approximates”

\[
n(r_1, \ldots, r_N) \approx \sum_m p(r_1, \ldots, r_N, c_m)
\]

Hartree-factorization:

\[
n(r_1, r_2, \cdots, r_N) = \sum_m p(r_m, c_m)
\]
Variational equation

interactions

\[ V[n] = \sum_{i>j} \int \int n_i(r_i)n_j(r_j)V(ij)dr_i dr_j \]

Kinetic energy functional = integral over quantum potential

\[ T[n] = \int n(r)Q[n(r)]dr \]

\[ T[n] = -\frac{\hbar^2}{2m} \sum_i \int \sqrt{n_i} \nabla^2_i \sqrt{n_i} dr_i = \sum_i T_W[n_i] \]

variation of total energy: “orbital free” version of DFT

\[ \delta \left\{ \sum_{i=1}^{N} \left( T_W[n_i(r_i)] + \sum_{j \neq i} \int \int n_i(r_i)n_j(r_j)V(ij)dr_i dr_j - \mu \left( \int n_i(r_i)dr_i - 1 \right) \right) \right\} = 0 \]

can include exchange/correlation for boson or fermion systems using approx. XC functionals
Euler Lagrange EOM

\[ \frac{\delta T_W[n_i(r_i)]}{\delta n_i(r_i)} + \sum_{j \neq i} \int V(ij)n_j(r_j)dr_j - \mu = 0. \]

Effective (statistical) potential for atom \( i \)

\[ V_i^e = Q(r_i) + V_e(r_i) + \sum_{j=1}^{N} V_p(r_i, r_j). \]

Sample each atomic density using points, move each sample point along gradient of total quantum energy

\[ \nabla_i E = - \sum_{j \neq i} \int (\nabla_i V(ij))n_j(r_j)dr_j - \nabla_i Q[n_i(r_j)] \]
Neₙ and Arₙ (n=4,13,19)

Quantum Hydrodynamic Approach for Molecular Clusters

Figure 1. The isodensity contour plots of the clusters at a value of 0.006. In the upper left is the Ar₄ cluster, in the upper right is the Ne₄, lower left has the Ar₅, and then bottom right is Ne₅. The axes are listed in atomic units.

Figure 3. Convergence of the 13- and 19-atom clusters of neon. The energy is in kJ/mol and the steps are given in millions.

Figure 4. Thirteen and 19-atom clusters with the quantum sample points in yellow overlaid on the classical equilibrium positions in black.

TABLE 1: Interatomic Distances for X                  

<table>
<thead>
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<th>Ar</th>
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The average potential energy corresponding to the classical equilibrium configuration, and they...
$V_{\text{quantum}} > V_{\text{classical}}$

- for 13 atom cluster: mean radius of quantum cluster about 3% > than classical
- 20% increase in volume.
- "spread of atoms due to uncertainty principle.
- internal quantum "pressure" of interior-most atom causes entire cluster to slightly swell for smaller closed (complete) shell clusters
Finite temperature theory \( \delta \Omega = 0 \)

grand ensemble \( Z(T, V, \mu) = Tr(e^{-\beta(H - \mu N)}) \)

\[
\Omega = -\frac{1}{\beta} \log(Tr[e^{-\beta(H - \mu N)}])
\]

Mermin: finite temperature DFT

\( \Omega[\hat{\rho}_T] = Tr[\hat{\rho}_T(K + V - \mu N + \frac{1}{\beta} \log \hat{\rho}_T)] \)

for any trial density: \( \Omega[\hat{\rho}_T] \geq \Omega[\hat{\rho}] \)
Entropy functional

\[ \Omega[n(r)] = F[n(r)] - \mu \int n(r) dr \]

\[ F[n(r)] = T_w[n(r)] + V[n(r)] + \frac{1}{\beta} S[n(r)] \]

Micro-canonical entropy:  \( S = k_B \log \Omega_{mc} \)

\[ S = -k_B \text{Tr}[\hat{\rho} \log \hat{\rho}] \]

\[ \mu = \frac{1}{\beta} \frac{\delta S}{\delta n} + Q(r) + V_{mf}(r) \]

\[ S[n(r)] = \frac{1}{\beta} \sum_i \int n_i(r_i) \log(n_i(r_i)) dr_i = \sum_i S[n_i] \]

Entropic “force”  \( \frac{\delta S}{\delta n_i} = \frac{1}{\beta} \left( \log(n_i(r_i)) + 1 \right) \)
Ground state energy vs. size.

FIG. 2: Various energetic contributions for quantum and classical Neon clusters versus cluster size, $N$. Key: $\langle \text{cl} \rangle =$ classical global potential minimum energy, $\langle \text{cl}+\text{qc} \rangle =$ zero-point energy corrections from Ref. [6], $\langle \text{E} \rangle =$ total energy, $\langle \text{Q} \rangle =$ quantum kinetic energy (from quantum potential).

$V_{eff} = V(r) + \frac{\hbar^2 \beta}{24m} V''(r)$
Fully QM vs. Q/C Corrected Energies.

TABLE I: Ground state vibrational energies for Ne$_n$ clusters
for our results compared to the results tabulated by Calvo et al. Ref. [6]

<table>
<thead>
<tr>
<th>Cluster</th>
<th>order</th>
<th>Energy (From Ref. [6] )</th>
<th>order</th>
<th>This work.</th>
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<td>17C</td>
<td>(1)</td>
<td>-11.0853 kJ/mol</td>
<td>(2)</td>
<td>-16.6336</td>
</tr>
<tr>
<td>17B</td>
<td>(2)</td>
<td>-11.0814</td>
<td>(3)</td>
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<td>(2)</td>
<td>-22.5496</td>
<td>(1)</td>
<td>-29.3524</td>
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</tbody>
</table>
Multiple “minima” separated by high barriers

approach an effectively sample a high-dimensional potential energy land-scape
Free energy vs. T for various small clusters

FIG. 3: The free energy of the different clusters vs. temperature. Error bars indicate numerical/statistical precision of each computed free energy value. Note the $T = 0$ values are offset to a common origin for comparison. The energies at $T = 0$ K for the three clusters are as follows: $F_0^{13} = -11.21$ kJ/mol, $F_0^{17} = -15.216$ kJ/mol, and $F_0^{37} = -39.03$ kJ/mol.
FIG. 4: Plots of the quantum, total potential, and entropic contributions to the total free energy vs. temperature for Ne$_{13}$.
Debye model: 
\[ U = 9Nk_B T \left( \frac{T}{T_D} \right)^3 \int_0^T \frac{T}{T_D} \frac{x^3}{e^x - 1} dx \]

\[ T_D = \frac{\hbar c_s}{2k_B} \left( 6N\pi V \right)^{-3} \]

\[ T_D(\text{Ne}) = 75K \]

FIG. 4: Plots of the quantum, total potential, and entropic contributions to the total free energy vs. temperature for the Debye model: 
\[ \text{Eff. Effects in the Debye model:} \]
\[ \text{Energy:} \]
\[ \text{This will be given by:} \]
\[ \tau \]
\[ \langle \frac{Q}{U} \rangle = 75K \]

FIG. 5: Internal energy comparison of the current results (•••) with the Debye model (—) at the following temperatures: 

\[ T_{k_B} \text{ vs. } \epsilon \]

FIG. 6: \((\langle Q \rangle/\langle U \rangle)\) vs. T. (Key: —: 13 atoms, •••: 17 atoms, ——: 37 atoms).
Negative heat capacity?

- **Numerical/Systematic Error?:**
  Cp<0 reported by D. Wales on the Ne13 cluster...not by Mandelshtam (filter diagonalization methods)

- **Physical Grounds:**
  Cp<0 has been reported for Na_{147} clusters and possibly neutron stars, certain types of blackholes, etc..


  Can show Cp<0 analytically for centrosymmetric potentials

  **Review:** D. Lynden-Bell Physica A 263, 293 (1999)

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**FIG. 5:** Internal energy comparison of the current results (•• ••) with the Debye model (−).
virial ratio: $<Q>/<U>$

FIG. 6: ($<Q>/<U>$) vs. T. (Key: —: 13 atoms, ···: 17 atoms, −·−: 37 atoms).
Conclusions

• “Bohm-inspired” approach for including quantum effects into a many-body system.

• To date this is the ONLY application of the Bohm/Hydrodynamic approach in a non-trivial system.

• Molecular dynamics “flavor” allows one to easily choose certain degrees of freedom to be described with varying degrees of “quantum” character. Much like path-integral MC or path-integral centroid dynamics.

• Finite temperature results: structural predictions and thermodynamics for rare-gas clusters are at least consistent with more standard approaches.

• Do not see “pre-melting” or “surface melting” (consistent w/Mandelshtam (PIMC)—different from classical simulation)

• Not restricted to magic number or closed shell clusters.
Group Publications/References


Thanks

• Bob Wyatt--inspiration and introduction to the topic.

• Jeremy Maddox, Sean Derrickson--2 PhD students crazy enough to pickup on this idea.

• Funding: National Science Foundation, Robert A Welch Foundation, TLC²

• J.S. Guggenheim Foundation (Fellow: 2007).

• Thanks: Irene Burghardt (ENS/Paris), David Wales (Cambridge).
“Entopic force” \[ \frac{\delta S}{\delta n_i} = \frac{1}{\beta} \left( \log(n_i(r_i)) + 1 \right) \]

Gaussian trial density: \[ n(x) = \sqrt{\frac{1}{2\pi \langle x^2 \rangle}} e^{-x^2/2\langle x^2 \rangle} \]

Harmonic osc:

\[ \langle F \rangle = \frac{1}{8m \langle x^2 \rangle} + \frac{m\omega^2}{2} \langle x^2 \rangle - \frac{1}{2\beta} \left( \log(2\pi \langle x^2 \rangle) + 1 \right) \]

\[ \delta \langle F \rangle = 0 \]

\[ \langle x^2 \rangle_{opt} = \frac{kT}{2m\omega^2} \left( 1 + \sqrt{1 + \left( \frac{\hbar\omega}{kT} \right)^2} \right) \]

\[ \langle x^2 \rangle_{exact} = \frac{\hbar}{2m\omega} \coth \left( \frac{\Theta_v}{2T} \right) \]

OK at high and low temperature--error is small
Univ. of Houston

- 2nd largest Univ. System in Tx
- 35,000 students on main campus
- More Pro-Football players than any other US University!
- High Tc Superconductivity discovered.
Famous Former Students

Carl Lewis

Clyde Drexler

Brent Spinor
Infamous Former Students

Ken Lay  (PhD Economics)

Bridget Boisselier  (PhD, Chemistry)

Tom DeLay  (BS-Biochemistry)

Former Enron CEO

Head of Clonaid, the "scientific wing" of the Raëlians.

Former Congressman and GOP Majority Leader