Solution of Eigenvalue Problems for Multi-Scale Phenomena by Quantum Monte Carlo Methods

Peter Nightingale

Department of Physics, University of Rhode Island, Kingston RI 02881, USA
INTRODUCTION

• Particle in semi-infinite square well of depth -1 and width 1
  Unbinding transition: reduce mass; at a critical mass the last bound state acquires infinite range and disappears

• Dimensionless binding energy of $^4\text{He}$ dimer (Hurly-Moldover $\phi_{00}$ potential): -0.0002 (2 mK)

• Schloss Ringberg (1997) cluster meeting panel discussion:
  find the number of excited states of small He clusters
Problem: Approximate $n$ energy eigenfunctions as linear combinations of $n$ basis functions $\beta_1, \ldots, \beta_n$

$$
\tilde{E} = \frac{\int \psi^*(R) \mathcal{H} \psi(R) dR}{\int \psi^*(R) \psi(R) dR}
$$

$$
\frac{\delta \tilde{E}}{\delta \psi(R)} \propto (\mathcal{H} - \tilde{E}) \psi(R)
$$

Stationary linear combination: gradient perpendicular to all basis functions

$$
\langle \beta_i | (\mathcal{H} - \tilde{E}) \sum_j d_j | \beta_j \rangle = 0
$$

$n \times n$ eigenvalue equation:

$$
N^{-1} \mathbf{H} \mathbf{d}^{(k)} = \tilde{E}_k \mathbf{d}^{(k)}
$$
with

\[ N_{ij} = \langle \beta_i | \beta_j \rangle \]
\[ H_{ij} = \langle \beta_i | \mathcal{H} | \beta_j \rangle \]

Yield:

<table>
<thead>
<tr>
<th>exact</th>
<th>approximate</th>
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<tbody>
<tr>
<td>( \psi^{(k)}(R) \approx \tilde{\psi}^{(k)}(R) = \sum_i \beta_i(R) d_i^{(k)} )</td>
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<tr>
<td>( E_k \lesssim \tilde{E}_k )</td>
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Optimization of linear prams

\( N^{-1}H \) from a small MC sample; zero-variance principle: exact eigenvectors in \( \text{span}(\beta_1, \ldots, \beta_n) \) no statistical errors
Numerical instability: \( N \) often nearly singular

Optimization of non-linear prams

Basis functions \( \beta_i \) depend on non-linear parameters. Optimize by minimization of

\[
\frac{\langle \tilde{\psi}^{(k)} | (H - \tilde{E}_k)^2 | \tilde{\psi}^{(k)} \rangle}{\langle \tilde{\psi}^{(k)} | \tilde{\psi}^{(k)} \rangle}
\]

Optimizations use small, fixed MC sample of $10^4$ configs, SCALA-PACK SVD, enhanced Levenbergh-Marquardt. (22 node Beowulf cluster)

Reduction of variational bias

Diffusion MC to obtain

$$|\tilde{\psi}^{(k)}\rangle \rightarrow |\tilde{\psi}^{(k)}\rangle(t) \equiv \exp(-t\mathcal{H})|\tilde{\psi}^{(k)}\rangle$$

[D.M. Ceperley and B. Bernu, J. Chem. Phys. 89, 6316 ('88)]

Pure DMC with large samples

Samples are generated with an optimized guiding function: maximize overlap with excited states; minimize fluctuations of re-weighting factors
$Ar_6$: $E_k$ vs projection $t/0.1$
FIG. 1. Ne: N=6 lowest 5 states
FIG. 2. N=4 VMC energies

$-|E_k|^\frac{1}{2}$

$k = 1$ : 

$k = 2$ :

$k = 3$ :

$k = 4$ :

$k = 5$ :

Kr 0.05 0.1 0.15 0.2 0.25 0.3 0.35

$m^{-\frac{1}{2}}$

Ar Ne He
FIG. 3. N=4 DMC energies at $t = 10 \times 0.1$

$-|E_k|^{1/2}$ vs $m^{-1/2}$ for $k = 1$ (diamonds), $k = 2$ (pluses), $k = 3$ (squares), $k = 4$ (times), and $k = 5$ (triangles). The data points correspond to the noble gases: Kr, Ar, Ne, and He.