Quantum Monte Carlo

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Pennsylvania State University
Monte Carlo Technique
Exploiting Physical Parallelism Using Supercomputers

Also in this issue:
- Expert System Building Tools
- Programming for Parallelism
- GaAs Technology
- Computer Science Accreditation
Monte Carlo methods

\[ I = \int_a^b y \, dx \]

\[ = \overline{y} (b-a) \]

\[ \approx \frac{\sum_{i=1}^{N} y_i}{N} (b-a) \]

\[ \frac{A_0}{A_0} = \frac{\pi}{4} \approx \frac{N \text{ in circle}}{N \text{ in square}} \]

Solitaire

[In the present article, the substance of the lecture is reproduced—with large additions, in which work commenced at the beginning of last year and continued after the lecture, during thirteen months up to the present time, is described—with results confirming the conclusions and largely extending the illustrations which were given in the lecture. I desire to take this opportunity of expressing my obligations to Mr. William Anderson, my secretary and assistant, for the mathematical tact and skill, the accuracy of geometrical drawing, and the unfailingly faithful perseverance in the long-continued and varied series of drawings and algebraic and arithmetical calculations, explained in the following pages. The whole of this work, involving the determination of results due to more than five thousand individual impacts, has been performed by Mr. Anderson.—K., Feb. 2, 1901.]

§ 1. The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds. I. The first came into existence with the undulatory theory of light, and

* Lecture delivered at the Royal Institution of Great Britain, on Friday, April 37, 1900.
† Communicated by the Author.
Schrödinger in Zürich on Dec. 1930
WAVE MECHANICS

Quantisation as a Problem of
Proper Values (Part I)

(Annalen der Physik (4), vol. 79, 1926)

§1. In this paper I wish to consider, first, the simple case of the hydrogen atom (non-relativistic and unperturbed), and show that the customary quantum conditions can be replaced by another postulate, in which the notion of "whole numbers", merely as such, is not introduced. Rather when integralness does appear, it arises in the same natural way as it does in the case of the node-numbers of a vibrating string. The new conception is capable of generalisation, and strikes, I believe, very deeply at the true nature of the quantum rules.

The usual form of the latter is connected with the Hamilton-Jacobi differential equation,

\( H(q, \frac{\partial S}{\partial q}) = E \).

A solution of this equation is sought such as can be represented as the sum of functions, each being a function of one only of the independent variables \( q \).

Here we now put for \( S \) a new unknown \( \psi \) such that it will appear as a product of related functions of the single co-ordinates, i.e. we put

\( S = K \log \psi. \)

The constant \( K \) must be introduced from considerations of dimensions; it has those of action. Hence we get

\( H(q, \frac{K \partial \psi}{\psi \partial q}) = E. \)

Now we do not look for a solution of equation \( (1') \), but proceed as follows. If we neglect the relativistic variation of mass, equation \( (1') \) can always be transformed so as to become a quadratic form (of \( \psi \) and its first derivatives) equated to zero. (For the one-electron problem
“The underlying physical laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

“It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

Diffusion and Green's Function
Quantum Monte Carlo Methods
James B. Anderson
Pennsylvania State University

\[ \langle E \rangle = \frac{\int \psi^2 \frac{\psi_0}{\psi_0} \, dV}{\int \psi_0^2 \, dV} \]

\[ \frac{\psi}{\delta E} = \frac{\hbar^2}{2m} \nabla^2 \psi - m \psi = -E \psi \]
\[ \frac{\partial \psi}{\partial E} = -i \nabla \psi \]
\[ \psi(x) = \left( \int \psi_0(x,x') \frac{V(x')}{E} \psi(x') \, dx' \right) \]

Corrections
\[ \Delta_{\text{QMC}} \]
Anderson 1976

Path Integral
\[ \text{PI-QMC} \]
Feynman +
DIFFUSION PNC

Inverse Energy

Schrödinger equation in imaginary time

\[
-\hbar \Psi \\
\frac{\partial \Psi}{\partial t} = \frac{\hbar^2}{2m} \nabla^2 \Psi - \sqrt{\Psi} = -\varepsilon \Psi
\]

Diffusion equation (with 1st order reaction)

\[
\frac{dc}{dt} = D \nabla^2 C - kC
\]
ÜBER DIE UMKREHRUNG DER NATURGESETZE

VON

E. SCHröDINGER

SONDERAUSGABE AUS DEN SITZUNGSBERICHTEN
DER PREußischen AKADEMIE DER WISSENSCHAFTEN
PHYS.-MATHEMATISCHE KLasse. 1931. IX

BERLIN 1931

VERLAG DER AKADEMY DER WISSENSCHAFTEN
IN KOMMISSION BEI WALTER DE GRUyTER U. CO.
Produkt irgendeiner Lösung von (1) in irgendeine Lösung von (2). Denn der erste Faktor in (14) ist nichts weiter als irgendeine Lösung von (1), charakterisiert durch \( \psi(x_o) \), ihre Werteverteilung zur Zeit \( t_o \). Analoges gilt vom 2. Faktor in (14) bezüglich der Gleichung (2). Ferner folgt leicht aus (1) und (2), daß ein Produkt zweier Lösungen ein zeitunabhängiges \( \int_{-\infty}^{+\infty} dx \ldots \) hat, mithin auf 1 normiert bleibt, wenn es zu irgendeiner Zeit auf 1 normiert war. (Diese Einschränkung muß natürlich gemacht werden: nur solche Lösungen dürfen verwendet werden, deren Produkt ein endliches \( \int_{-\infty}^{+\infty} dx \ldots \) hat, so daß man es auf 1 normieren kann.) Alsdann darf man noch innerhalb derjenigen Zeitspanne, für welche das Lösungsprodukt regulär bleibt, irgende zwei Zeitpunkte \( t_o, t \), beliebig wählen als diejenigen, für welche die Wahrscheinlichkeitsdichte beobachtet sei (natürlich so beobachtet, wie die Werte des Produktes eben sind). Das Produkt liefert dann die Wahrscheinlichkeitsdichte für die Zwischenzeit.


Einleitung. Wenn für ein diffundierendes oder in Brownscher Bewegung begriffenes Teilchen die Aufenthaltswahrscheinlichkeit im Abszissenbereich \((x; x + dx)\) zur Zeit \(t_0\)
\[
w(x, t_0) \, dx
\]
gegeben ist,
\[
w(x, t_0) = w_0(x),
\]
so ist sie für \(t > t_0\) diejenige Lösung \(w(x, t)\) der Diffusionsgleichung
\[
D \frac{\partial^2 w}{\partial x^2} = \frac{\partial w}{\partial t},
\]
welche für \(t = t_0\) der vorgegebenen Funktion \(w_0(x)\) gleich wird. — Über Probleme dieser Art, mit vielen möglichen Komplikationen und Variationen, die durch spezielle Versuchsanordnungen und Beobachtungsmethoden nahegelegt waren, gibt es eine umfangreiche Literatur, wobei das System, um das es sich handelt, gar nicht ein diffundierendes Teilchen zu sein braucht, sondern beispielsweise die Elektrometernadel bei der K. W. F. Kohlrauschischen Anordnung zur Messung der Schwingungsschwellen, und an Stelle der Gleichung (1) ihre Verallgemeinerung tritt, die sogenannte Fokker-Plancksche partielle Differentialgleichung für das betreffende, irgendwelchen Zufallseffekten ausgesetzte System.

Solche Systeme geben nun zu einer Klasse von Wahrscheinlichkeitsproblemen Anlaß, die bisher keine oder wenig Beachtung gefunden hat und die schon rein mathematisch dadurch von Interesse ist, daß die Antwort nicht durch eine Lösung der Fokkerschen Gleichung geliefert wird, sondern, wie sich zeigen wird, durch das Produkt der Lösungen zweier adjungierter Gleichungen, wobei sich …
THE MONTE CARLO METHOD

NICHOLAS METROPOLIS AND S. ULAM
Los Alamos Laboratory

We shall present here the motivation and a general description of a method dealing with a class of problems in mathematical physics. The method is, essentially, a statistical approach to the study of differential equations, or more generally, of integro-differential equations that occur in various branches of the natural sciences.

Already in the nineteenth century a sharp distinction began to appear between two different mathematical methods of treating physical phenomena. Problems involving only a few particles were studied in classical mechanics, through the study of systems of ordinary differential equations. For the description of systems with very many particles, an entirely different technique was used, namely, the method of statistical mechanics. In this latter approach, one does not concentrate on the individual particles but studies the properties of sets of particles. In pure mathematics an intensive study of the properties of sets of points was the subject of a new field. This is the so-called theory of sets, the basic theory of integration, and the twentieth century development of the theory of probabilities prepared the formal apparatus for the use of such models in theoretical physics, i.e., description of properties of aggregates of points rather than of individual points and their coordinates.

Soon after the development of the calculus, the mathematical apparatus of partial differential equations was used for dealing with the problems of the physics of the continuum. Hydrodynamics is the most widely known field formulated in this fashion. A little later came the treatment of the problems of heat conduction and still later the field theories, like the electromagnetic theory of Maxwell. All this is very well known. It is of course important to remember that the study of the
DIFFUSION DMC

Inverse energy

Schrödinger equation in imaginary time

\[ -i \hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \psi - \sqrt{\psi} = - \xi \psi \]

Diffusion equation (with 1st order reaction)

\[ \frac{dC}{dt} = D \nabla^2 C - kC \]
Random walk $\leftrightarrow$ Diffusion

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Einstein 1904

$$D = \frac{1}{2} \frac{(\Delta x)^2}{\Delta t}$$
\[
\frac{\partial Y}{\partial t} = D \frac{\partial^2 Y}{\partial x^2} - k_2 Y
\]
\[ \frac{\partial \psi}{\partial t} = \frac{i}{2\mu} \frac{\partial^2 \psi}{\partial x^2} - \sqrt{\psi} \]

\[ \psi = A(t) \sin \frac{\pi x}{L} \]
\[ \frac{\partial \psi}{\partial t} = \frac{-i}{\hbar} \frac{\partial^2 \psi}{\partial x^2} - \frac{1}{2} \psi \]

earlier

\[ \psi = A(t) \sin \frac{n\pi x}{L} \]
Particle in a box

\[ N_\psi \]

\[ x/L \]

- calc. by RW
- exact
Determining energies

$$\frac{d\psi}{d\tau} = \frac{1}{2} \nabla^2 \psi - V \psi = -E \psi$$

$$\sum_{\tau} \left( \frac{d\psi}{d\tau} \right) = \int \frac{1}{2} \nabla^2 \psi - V \psi = -E \psi \quad dx$$

$$\frac{dN}{d\tau} = -\sigma N$$

$$E = -\frac{1}{N} \frac{dN}{d\tau}$$

For no nodes

$$\int_{\frac{1}{2} \nabla^2 \psi - \int V \psi = -E \int \psi \quad dx$$

$$\psi$$

$$E = \frac{\int V \psi}{\int \psi} = \bar{\psi}$$

$$= \frac{\psi}{\psi^*} \quad \text{Psuedas}$$
sources of error

→ Finite time steps
  numerical - roundoff
  random number quality
  not 'steady state'
  minor prejudices
→ node locations
→ statistical or sampling error

\[ E = \overline{\sqrt{i}} = \frac{1}{N} \sum_{i} \sqrt{i} \]

\[ \sigma_{\text{mean}} = \frac{1}{\sqrt{N}} \sigma_i \]

\[ \sim \frac{1}{\sqrt{N}} \sigma_i \]

\[ \sim \frac{1}{\sqrt{t}} \sigma_i \]

\[ \sim \frac{1}{\sqrt{\langle E \rangle}} \sigma_i \]
$\text{H}_3^+$

\[ \text{add importance sampling} \\
1981 \quad -1.3439 \quad \pm 0.0002 \\
1982 \quad -1.34376 \quad \pm 0.00003 \\
\text{add Green's Function} \\
1988 \quad -1.34387 \quad \pm 0.00005 \\
\text{add cancellation} \\
1992 \quad -1.343835 \quad \pm 0.000001 \\
\]

First to reach $\pm 1$ microhartree for a polyatomic \[ \pm 0.0006 \text{ kcal/mole} \]
Adding Importance Sampling

\[ \dfrac{\delta \psi}{\delta \varepsilon} = \dfrac{1}{2} \psi^2 \gamma - \sqrt{\psi} \]

multiply by \( \gamma \), let \( f = \frac{\psi}{\gamma} \), rearrange

\[ \dfrac{\delta f}{\delta \varepsilon} = \dfrac{1}{2} \psi f' - \gamma \cdot (f \nabla \ln \gamma) - \dfrac{H \gamma}{\gamma} \cdot f \]

diffuse drift multiply

\[ \dfrac{H \gamma}{\gamma} = \varepsilon_{\text{local}} = - \dfrac{1}{2} \psi \frac{\psi}{\gamma} + \alpha \]

\[ \varepsilon = \varepsilon_{\text{local}} = \frac{\psi}{\gamma} \frac{\varepsilon_{\text{local}}}{\gamma} + \alpha \]

\[ \psi = \text{easily single-determinant, multiply by various terms} \]
Green's Function QMC

\[ \alpha \psi = -E \psi \]

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

Rearrange to

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

Where \( k^2 = -\frac{2mE}{\hbar^2} \)

i.e. \( \psi(x) \to 0 \) as \( x \to \infty \)

\[ \psi(x) = \int G_0(x, x') \frac{V(x')}{E} \psi(x') \, dx' \]

- Given set of \( \alpha \)s with specific positions \( x' \)
- Multiply weights by \( \frac{1}{\alpha} \)
- Sample \( G_0(x, x') \) for \( x, \) move to \( x' \)
- Repeat to approach \( \psi(x) \) distribution
- Continue for additional samples of \( \psi(x) \)
no node

previously large $\Delta$ shift to keep at negative

for $U \in$ positive

small steps

now large steps, low serial correlation

also better trial function faster computer

$E = -1.343835 \text{ au}$

$\pm 0.000001$
Node locations

2-5 A Vibrating Membrane

Powder that is sprinkled on a vibrating drumhead will collect at the nodes, where the vibrations are the weakest. The photographs illustrate six of the normal modes of a circular drumhead.
Fixed node method

"Variational" with respect to node locations

incorrect node

\[ A \quad \text{and} \quad E_A = E_A' \]

Correct node

\[ B \quad \text{and} \quad E_B = E_B' \]

\[ E_A \geq E_B \]

Exact solution within A

Good locations lead to excellent energies

Find good nodes where you can

i.e., SCF etc.
“The dreaded Sign Problem In Quantum Monte Carlo”
SPECIAL DOUBLE ISSUE

Grand Challenges to Computational Science

Guest Editor
C.E. Rhoades
Figure 1. a) Potential energies for particle in two-dimensional box. b) Illustration of possible nodes for first excited state. c) Schematic diagram of the effect of cancellation of a positive function (solid line) by its inverse (dotted line) to yield the excited state.
Barrier Height for $H + H_2 \rightarrow H_2 + H$

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<td>Liu</td>
<td>Liu</td>
<td>C&amp;A</td>
<td>BR &amp; L</td>
<td>D&amp;A</td>
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<td>QMC</td>
<td>QMC</td>
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</tbody>
</table>

- March
- Anderson
- Engelage
- Alder
- Brack
- Reynolds
- Latimer
- Diedrich
- Anderson

10.4 - 10.2 - 10.28 - 10.20

9.8 - (est.) - 9.65 - (est.) - 9.70 - 9.61 ± 0.01

9.4 - "Fixed node estimate"

9.2 - "Exact"

"Exact cancellation scheme"
Accuracy of EQMC calculation:
\[ \pm 0.000014 \text{ or } 3 \text{ cm}^{-1} \]

Clementi et al., Chem. Rev. 91, 679 (1991), estimated that an analytic variational calculation for H-H-H accurate to within 10 cm\(^{-1}\) of the exact value “would call for somewhere around 3500 years” on a computer similar to the one we used.

<table>
<thead>
<tr>
<th>EQMC</th>
<th>CI</th>
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<tbody>
<tr>
<td>3 months</td>
<td>2 millennia</td>
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</table>

Experiment ahead of theory?  
Theory ahead of experiment?  
Forever?
Book Review


This book, Volume 15 of the series _Understanding Chemical Reactivity_, consists of eight chapters reviewing different fields of applied quantum chemistry. Most of the book covers applications of high accuracy methods, with some chapters focusing on specific topics such as applications with specific molecules or reactions.

The first chapter, by J. B. Anderson, deals with the exact quantum Monte Carlo method (QMC) and its applications to systems of a few electrons. The chapter gives a nice introduction to QMC methods and the results presented are impressive but seem unnecessarily precise for chemistry.

In Chapter 3, D. M. Chupman presents calculations of magnetic hyperfine coupling constants for atoms and small molecules, and these are compared with experimental data.

In Chapter 4, L. A. Curtiss and K. Raghavachari review the Gaussian-2 (G2) procedure for calculating molecular energies. This method uses perturbation theory to fourth order, MP4, to estimate correlation effects. The performance of the method is tested on a set of systems containing first and second row atoms and some modifications of the G2-theory are discussed.

In Chapter 5, Raghavachari and Curtiss review applications of quantum chemical techniques to the study of small clusters of the elements B, Al, C, Si, P, and S. Geometries, binding energies, and vibrational frequencies are presented. The level of theory used ranges from HF/3-21G* to G2-theory.

The authors present vertical excitation energies and oscillator strengths for a number of organic molecules. For a few systems, 0-0 transition energies and emission spectroscopic data are also calculated.

In general the book is well written and I expect it to be of interest to many spectroscopists and applied quantum chemists. However, because of the high price, I can recommend it only to libraries.

Robert Bergström

<table>
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<tr>
<th>Theoretical method(^b)</th>
<th>Current computational dependence on molecular size, (M)</th>
<th>Current estimate of maximum feasible molecular size</th>
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<tr>
<td>FCI</td>
<td>Factorial</td>
<td>2 Atoms</td>
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<tr>
<td>CCSD(T)</td>
<td>(M^7)</td>
<td>8–12 atoms</td>
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<tr>
<td>CCSD</td>
<td>(M^6)</td>
<td>10–15 atoms</td>
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<tr>
<td>MP2</td>
<td>(M^5)</td>
<td>25–50 atoms</td>
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<tr>
<td>HF, KS-DFT</td>
<td>(M^2–M^3)</td>
<td>50–200 atoms</td>
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<tr>
<td>FN-QMC</td>
<td>(M^3)</td>
<td>250–500 atoms</td>
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</table>

\(^a\)Adapted from Head-Gordon (13) with additions from Shlyakhter et al (12).

\(^b\)FCI, CCSD(T), full configuration interaction coupled cluster method with perturbative triple excitation; CCSD, coupled cluster method; MP2, Møller-Plesset perturbation 2; HF, KS-DFT, Hartree-Fock, Kohn-Sham–density functional methods; FN-QMC, Fixed-node–quantum Monte Carlo.
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<th>Method type and basis</th>
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<td>BLYP/MP2 6-31G</td>
<td>0.0</td>
<td>0.6</td>
<td>3.8</td>
<td>ring</td>
</tr>
<tr>
<td>rosemig</td>
<td>BLYP 6-31G</td>
<td>0.0</td>
<td>1.1</td>
<td>3.4</td>
<td>ring</td>
</tr>
<tr>
<td>wdp</td>
<td>BLYP 6-31G(d,p)</td>
<td>0.0</td>
<td>1.5</td>
<td>3.3</td>
<td>ring</td>
</tr>
<tr>
<td>gmr</td>
<td>BLYP 6-31G*</td>
<td>0.0</td>
<td>1.1</td>
<td>3.4</td>
<td>ring</td>
</tr>
<tr>
<td>gmr</td>
<td>B3LYP 6-31G*</td>
<td>0.6</td>
<td>0.0</td>
<td>1.4</td>
<td>bowl</td>
</tr>
<tr>
<td>gmr</td>
<td>B3LYP 6-31G*</td>
<td>0.0</td>
<td>0.4</td>
<td>2.3</td>
<td>ring</td>
</tr>
<tr>
<td>gmr</td>
<td>B-PW91 6-31G*</td>
<td>0.5</td>
<td>0.0</td>
<td>0.8</td>
<td>bowl</td>
</tr>
<tr>
<td>gmr</td>
<td>B3-PW91 6-31G*</td>
<td>0.8</td>
<td>0.0</td>
<td>0.7</td>
<td>bowl</td>
</tr>
<tr>
<td>Coupled Cluster</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>btwk</td>
<td>CCSD</td>
<td>1.5</td>
<td>0.0</td>
<td>0.7</td>
<td>bowl</td>
</tr>
<tr>
<td>btwk</td>
<td>CCSD(T) cc-pVDZ</td>
<td>1.7</td>
<td>0.0</td>
<td>0.0</td>
<td>bowl/cage</td>
</tr>
<tr>
<td>tbwk</td>
<td>CCSD(T) cc-pVDZ</td>
<td>2.8</td>
<td>0.0</td>
<td>0.6</td>
<td>bowl</td>
</tr>
<tr>
<td>tbwk</td>
<td>CCSD(T) + est.</td>
<td>2.6</td>
<td>0.2</td>
<td>0.0</td>
<td>cage</td>
</tr>
<tr>
<td>Quantum Monte Carlo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gmr</td>
<td>pspQMC</td>
<td>1.1</td>
<td>0.0</td>
<td>2.2</td>
<td>bowl</td>
</tr>
<tr>
<td>this work</td>
<td>aeQMC</td>
<td>1.0</td>
<td>0.0</td>
<td>2.0</td>
<td>bowl</td>
</tr>
</tbody>
</table>
$C_2O$

ring, bowl, or cage.
Some examples of larger systems from other labs:

REACTION PATHS FOR OXIDATION OF CYCLOPENTADIENE (36-VALENCE ELECTRONS)

Cyclopentadiene C5H6 is formed during the combustion process of aromatic compounds such as benzene (30, 31). Its further oxidation is a matter of great interest for the elucidation of combustion processes. In a recent study, Grossman et al. (32) examined the oxidation of cyclopentadiene to 2-cyclopentenone and 

![Chemical Structures]

Figure 2: Reaction pathways for oxidation of cyclopentadiene to cyclopentenone. From reference 32 by permission.
Cyclo-octatetraene (COT) with its eight $\pi$ electrons is not aromatic and thus has a nonplanar $D_{2d}$ structure. It has long been known that COT can undergo inversion between the degenerate $D_{2d}$ structures. With new techniques it is now possible to measure barrier heights experimentally to high accuracy—thereby challenging

**Figure 5** $D_{2h}$ transition state for cyclo-octatetraene inversion.

**TABLE 2** Energy differences in eV from $D_{2d}$ ground state of cyclooctatetraene to singlet and triplet transition states$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>TS singlet$^b$</th>
<th>TS triplet$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GVB</td>
<td>1.40</td>
<td>1.19</td>
</tr>
<tr>
<td>LDA</td>
<td>0.95</td>
<td>0.67</td>
</tr>
<tr>
<td>BLYP</td>
<td>0.85</td>
<td>0.52</td>
</tr>
<tr>
<td>BPW91</td>
<td>0.88</td>
<td>0.50</td>
</tr>
<tr>
<td>QMC</td>
<td>0.61 (7)</td>
<td>0.87 (7)</td>
</tr>
<tr>
<td>Expt</td>
<td>0.61 (7)</td>
<td>0.95 (7)</td>
</tr>
</tbody>
</table>

$^a$Reprinted from reference 35 by permission of the publisher. Numbers in parentheses indicate statistical error in last digit.

$^b$TS, Transition state; GVB, generalized valence bond; LDA, local density approximation; BLYP, hybrid method (Becke, Lee, Yang, Perdew); BPW91, Becke, Perdew, Wang, 1991; QMC, quantum Monte Carlo; Expt, experimental measurement.
DOPED HELIUM CLUSTERS (TO 500 PARTICLES)

Small superfluid $^4$He droplets have attracted increasing interest recently. Molecules can be picked up (adsorbed or absorbed) easily by helium droplets in molecular beams to form doped helium clusters. With laser spectroscopic techniques, the dopant molecules can then be studied with high resolution at extremely low temperatures. Experiments show free rotor spectra for the molecules picked up by $^4$He$_N$ droplets, in contrast to nonsuperfluid fermionic $^3$He$_N$ clusters for which rotationally resolved spectra could not be obtained (50–53). With this technique it has become possible to form and study spectroscopically van-der-Waals clusters inside helium droplets (53, 54).

In a thorough theoretical description of doped helium clusters, the quantum nature of the clusters and the intrinsic many-body interactions inside the cluster pose a serious challenge. The QMC method is particularly well suited for this task, and it allows one to obtain the ground-state wave function exactly, provided that the interactions inside the cluster are known. Besides the determination of the structure of doped helium clusters, QMC-based methods can be used to investigate the influence of the cluster environment on the spectral properties of the dopant.
POSITRON COMPLEXES \([\text{OH}, \text{Ps}], [\text{CH}, \text{Ps}], \text{AND} [\text{NH}_2, \text{Ps}]\)
\section*{(8–10 ELECTRONS AND 1 POSITRON)}

The leptonic structures and stabilities of the ground state and several excited states of positronium hydride PsH (where Ps = e\(^+\), e\(^-\)) have been successfully treated in several VQMC and DQMC studies (63). The ground states of several positron-molecule and positronium-atom complexes involving first-row atoms have been similarly treated in VQMC and FN-DQMC studies (64, 64a). An example of these kinds of calculations is the work recently reported by Bressanini et al (65) for the systems \([\text{OH}, \text{Ps}], [\text{CH}, \text{Ps}],\) and \([\text{NH}_2, \text{Ps}]\), which each contain 8–10 electrons and 1 positron, as well as heavier nuclei.

\textbf{TABLE 4} Variational and Fixed-node diffusion quantum Monte Carlo positron affinity (PA) and positronium binding energy (BE) for the complexes [M,Ps]

<table>
<thead>
<tr>
<th>Molecule and state</th>
<th>(E_{\text{DQMC}})</th>
<th>(PA_{\text{DQMC}})</th>
<th>(BE_{\text{DQMC}})</th>
<th>(EA_{\text{DQMC}})</th>
<th>(EA_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OH}) (^2\Pi)</td>
<td>-75.7213(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{OH}^-) (^2\Pi)</td>
<td>-75.722(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{OH}, \text{Ps}]) (^2.1\Sigma^+)</td>
<td>-75.9815(9)</td>
<td>0.1941(10)</td>
<td>0.0102(12)</td>
<td>0.0661(9)</td>
<td>0.0673</td>
</tr>
<tr>
<td>(\text{CH}) (^2\Pi)</td>
<td>-38.4630(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CH}^-) (^3\Sigma)</td>
<td>-38.5087(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{CH}, \text{Ps}]) (^2-3\Sigma^-)</td>
<td>-38.7291(3)</td>
<td>0.2200(4)</td>
<td>0.0161(6)</td>
<td>0.0461(5)</td>
<td>0.0456</td>
</tr>
<tr>
<td>(\text{NH}_2) (^2\Pi_1)</td>
<td>-55.7428(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{NH}_2^-) (^1\Sigma_1)</td>
<td>-55.7218(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{NH}_2, \text{Ps}]) (^2-3\Sigma_1)</td>
<td>-55.9282(5)</td>
<td>0.2277(7)</td>
<td>0.0056(9)</td>
<td>0.0279(9)</td>
<td>0.0272</td>
</tr>
</tbody>
</table>

\(^*\)FN-DQMC and experimental electron affinity (EA) for the molecules OH, CH, and NH\(_2\). Energies in Hartrees. From Bressanini et al (65). Numbers in parentheses indicate statistical error in last digit.
METALLO-CARBOHEDRENES (16 OUTER ELECTRONS FOR TiC)

The discovery of the titanium carbon cluster Ti₈C₁₂ by Guo et al (73) has initiated a large number of experimental (74, 75) and theoretical (76–78) investigations of this and similar compounds that have become known as metallo-carbohedrenes (Met-Cars). The proposed structures for this and related clusters, a cagelike pentagonal dodecahedron and a tetracapped tetrahedral cage structure, can explain their unusual stability (73, 78).

While electronic-structure calculations on Met-Cars are possible with DFT methods, the number of electrons is currently too large for high-level ab initio methods such as CCSD(T), multireference configuration interaction (MRCI), or FN-DQMC. The diatomic TiC is the simplest compound for studying bonding in Met-Cars and comparing methods as an initial step toward reliable theoretical investigation of Ti₈C₁₂ and similar clusters.

S. Sokolov
A. Züchter
(2000)
WATER CLUSTERS \([\text{TO} (\text{H}_2\text{O})_{10}]\)

Water clusters have been the focus of considerable interest in recent years. One of the objectives is to understand how the properties of \((\text{H}_2\text{O})_n\) evolve toward the condensed phase. Small water clusters offer unique opportunities to study in detail, experimentally and theoretically, the structure and dynamics of the hydrogen-bonded network that determine the properties of liquid water.

Figure 7  Water trimer cyclic \((\text{left})\) and water hexamer cage \((\text{right})\) structures. From reference 88 by permission.
BAND STRUCTURE OF SILICON (64 VALENCE ELECTRONS)

In recent years, the QMC method has increasingly been applied to solids. QMC has many features that make it attractive for solid-state calculations: it scales reasonably with the number of explicitly treated electrons, and it can reliably calculate >90% of the electron correlation energy. It can be expected that QMC yields accurate cohesive energies. In QMC, as in other methods, the infinite nature of the solid is accounted for by periodic boundary conditions.

### Table 5

<table>
<thead>
<tr>
<th>Band</th>
<th>DQMC</th>
<th>HF</th>
<th>GW</th>
<th>LDA</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{25}$</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\Gamma_{15}$</td>
<td>3.70</td>
<td>8.0</td>
<td>3.36</td>
<td>2.55</td>
<td>3.40, 3.05</td>
</tr>
<tr>
<td>$\Gamma_{1}$</td>
<td>4.57</td>
<td>9.0</td>
<td>3.89</td>
<td>3.19</td>
<td>4.23, 4.1</td>
</tr>
<tr>
<td>$\Gamma_{1}'$</td>
<td>-13.58</td>
<td>-18.9</td>
<td>-11.95</td>
<td>-11.95</td>
<td>-12.5 $\pm$ 0.6</td>
</tr>
<tr>
<td>$X_{1c}$</td>
<td>1.51</td>
<td>5.3</td>
<td>1.43</td>
<td>0.63</td>
<td>1.25</td>
</tr>
<tr>
<td>$X_{4}$</td>
<td>-3.35</td>
<td>-4.7</td>
<td>-2.93</td>
<td>-2.84</td>
<td>-3.3 $\pm$ 0.2, -2.9</td>
</tr>
<tr>
<td>$X_{1y}$</td>
<td>-8.79</td>
<td>-12.5</td>
<td>-7.95</td>
<td>-7.81</td>
<td>n/a</td>
</tr>
<tr>
<td>$L_{1c}$</td>
<td>2.51</td>
<td>6.5</td>
<td>2.19</td>
<td>1.44</td>
<td>2.4 $\pm$ 0.15, 2.1</td>
</tr>
<tr>
<td>$L_{3}$</td>
<td>4.55</td>
<td>8.7</td>
<td>4.25</td>
<td>3.31</td>
<td>4.15 $\pm$ 0.2</td>
</tr>
<tr>
<td>$L_{3}'$</td>
<td>-1.32</td>
<td>-2.0</td>
<td>-1.25</td>
<td>-1.19</td>
<td>-1.2 $\pm$ 0.2, -1.5</td>
</tr>
<tr>
<td>$L_{1y}$</td>
<td>-7.81</td>
<td>-11.1</td>
<td>-7.14</td>
<td>-6.99</td>
<td>-6.7 $\pm$ 0.2</td>
</tr>
<tr>
<td>$L_{2}'$</td>
<td>-11.05</td>
<td>-15.4</td>
<td>-9.70</td>
<td>-9.61</td>
<td>-9.3 $\pm$ 0.4</td>
</tr>
</tbody>
</table>

*The DQMC entries have a statistical error of 0.2 eV. Republished from 100, by permission.
Abbreviations: DQMC, diffusion quantum Monte Carlo; HF, Hartree-Fock; GW, Green's function/treated Coulomb; LDA, local density approximation; Expt, experimental data; n/a, not applicable.
CUBIC BORON NITRIDE CRYSTALS (216 VALENCE ELECTRONS)

Malatesta et al (108) have carried out VQMC calculations to investigate the cohesive properties of cubic boron nitride crystals. These PP-VQMC calculations were made for simulation regions of \(2 \times 2 \times 2\) and \(3 \times 3 \times 3\) unit cells of two atoms (B-N) with totals of 64 and 216 valence electrons, respectively. The properties calculated were found in good agreement with experiments.

Cubic boron nitride is a prototypical heteropolar system, similar in many ways to diamond. The calculation procedures that were successful in earlier calculations for diamond were similarly successful for boron nitride. The pseudopotentials were of the Hamann-Schlüter-Chiang type (109) used in earlier calculations.

<table>
<thead>
<tr>
<th>Ground-state energy</th>
<th>VMC (eV)</th>
<th>LDA (eV)</th>
<th>Expt(^b) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B atom</td>
<td>(-71.31 \pm 0.014)</td>
<td>(-70.55)</td>
<td></td>
</tr>
<tr>
<td>N atom</td>
<td>(-266.57 \pm 0.014)</td>
<td>(-264.95)</td>
<td></td>
</tr>
<tr>
<td>cBN (2 \times 2 \times 2)</td>
<td>(-349.11 \pm 0.09)</td>
<td>(-348.60)</td>
<td></td>
</tr>
<tr>
<td>cBN (3 \times 3 \times 3)</td>
<td>(-350.70 \pm 0.08)</td>
<td>(-350.54)</td>
<td></td>
</tr>
<tr>
<td>cBN (size-corrected)</td>
<td>(-351.06 \pm 0.08)</td>
<td>(-350.90)</td>
<td></td>
</tr>
<tr>
<td>Cohesive energy</td>
<td>12.85 \pm 0.09</td>
<td>15.07</td>
<td>12.9–13.0</td>
</tr>
</tbody>
</table>

\(^a\)Calculations are by Malatesta et al (108). Energies are in eV for B and N and in eV per pair of atoms for the crystal. Calculated cohesive energy includes added zero-point energy of 0.33 eV per pair.

\(^b\)Experimental data are from reference 110.
DIAMOND STRUCTURE SILICON (TO 1000 VALENCE ELECTRONS)

The largest system treated to date in QMC calculations is a 250-atom extended system of silicon atoms in a diamond structure. These calculations were carried out first by Williamson et al (111) with VQMC calculations, using pseudopotentials and a plane wave basis set for the four valence electrons of each atom. Simulation cell sizes were varied in $n \times n \times n$ multiples of the primitive unit cell with $n = 2, 3, 4$, and 5 corresponding to 16, 54, 128, and 250 atoms or 64, 208, 512, and 1000 electrons, respectively. With these calculations, Williamson et al tested a new model periodic Coulomb interaction and found it to be far superior to the

![Graph showing energy per atom vs. system size](image)

**Figure 8** Variation of energy (per atom) with simulation cell size $n$ in calculations by Williamson et al (111) for silicon crystal. The values $n = 2, 3, 4$, and 5 correspond to 64, 208, 512, and 1000 valence electrons in the cell.
J. CARLSON, J. MORALES, JR.,
V. R. PANDHARIPANDE, &
D. E. RAVENHALL

Quantum Monte Carlo calculations of neutron matter


Pure neutron matter is not likely to be found in any of the earth’s laboratories, but it has been found to exist as the material of neutron stars. It presents an interesting and difficult many-body problem which may be attacked by QMC methods. In this paper the authors report variational, approximate fixed-node, and released-node QMC calculations for uniform neutron matter in a three-dimensional box with periodic boundary conditions. These allow the determination of the energy \(E(\rho)\) as a function of the neutron density \(\rho\) for a realistic two-neutron interaction expression. The results are used to assess the accuracy of earlier variational approaches.

The system treated was that of 14 neutrons in a cube at densities in the range of 1/4 to 3/2 the density \(\rho_0\) typical for nuclear matter. Most of the calculations were done for the Argonne v8' two-body interaction potential. The trial wavefunction was a correlated Slater function, identical for the variational and diffusion calculations, specifying the nodes and used in importance sampling. Corrections were made for the effects of finite box dimensions. The released-node calculations were limited to very short time intervals especially at the higher densities.

The energies \(E(\rho)\) found in the diffusion QMC calculations were 3 to 10% lower than those of the variational QMC. The released-node results, with relatively large statistical errors, were not significantly different from the fixed-node results. The energies determined for the lower densities were estimated to be accurate within 2% and those for the higher densities somewhat less accurate. The results showed earlier predictions to be generally correct. Comparisons of results from variational chain summations (VCS) indicated an overall accuracy of about 10% for that method.
A. ASPURU-GUZIK, O. EL AKRAMINE,
J. C. GROSSMAN, & W. A. LESTER, JR.

Quantum Monte Carlo for electronic excitations of
free-base porphyrin


With 216 electrons, the free-base porphyrin C_{20}N_{4}H_{14} presents
a challenge to ab initio electronic structure calculations. Since it
is at the center of the mechanism of photosynthesis, as well as
several other biological processes, there has been much interest in
this molecule and its electronic spectrum, but despite a number
of earlier studies, important questions remain open. This paper
provides the most accurate calculations to date of energy levels of
states involved in several allowed and non-allowed transitions seen
in the spectrum. These were obtained in all-electron fixed-node
diffusion QMC calculations for the singlet ground states, the first
excited singlet state 1^1B_{2u}, and the lowest triplet state 1^3B_{2u}.
The trial functions for importance sampling were based on Hartree-
Fock and modified Hartree-Fock determinants using a 6-311G**
basis set and Jastrow correlation factors. The calculations were
carried out for thousands of hours to reduce statistical error to
about 0.1 eV. At -988.985(3) hartrees, the computed ground state
energy was 5.6 hartrees lower than the Hartree-Fock energy and
2.3 hartrees lower than the coupled-cluster CCSD(T) energy. The
computed excitation energies were in good agreement with experi-
mental values: for 1^1B_{2u}, 2.45(8) eV versus experimental values of
2.42 and 2.46 eV; for 3^3B_{2u}, 1.60(10) eV versus an experimental
value of 1.58 eV. These clearly demonstrate the suitability of dif-
fusion QMC for predicting energetics of large biological molecules.
Excitations in photoactive molecules from quantum Monte Carlo


Among the several quantum approaches to the accurate description of excitation processes in biological systems, the most promising candidates are: CASPT2, complete active space second-order perturbation theory; TDDFT, time-dependent density functional theory; ROKS, the restricted open-shell Kohn-Sham method; and QMC, quantum Monte Carlo. Each of these has its disadvantages. CASPT2 scales poorly with system size and is limited to smaller molecules. ROKS and TDDFT can be applied to very large systems but they may or may not be adequate for photoactive molecules. QMC scales favorably with system size but is computationally expensive. The authors address these issues in this paper with fixed-node diffusion QMC calculations for ground and excited states for prototypical photosensitive molecules, and comparison calculations by CASPT2, TDDFT, and ROKS methods.

The species chosen were formaldehyde (CH$_2$NE), formaldehyde (CH$_2$O), and a protonated Schiff base (C$_2$H$_4$NH$^+$) serving as a model for the retinal chromophore. The all-electron calculations were carried out with trial functions made up of linear combinations of Slater determinants, with Jastrow correlation factors optimized to minimize the average of energies for ground and excited states, using a fixed set of orbitals available for both. This was found to be important in obtaining accurate excitation energies. Transitions were examined along isomerization paths for each of the species, and comparisons of results were made for a variety of configurations.

Important differences in several of the predictions were observed. QMC and TDDFT results were in general agreement except for differences in the isomerization path for the Schiff base model. ROKS was found to exhibit large differences for lower symmetry structures. A limited number of comparisons showed the CASPT2 and QMC results to be qualitatively similar but with lower excitation energies for CASPT2.
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Quantum Monte Carlo is a large class of computer algorithms that simulate quantum systems with the idea of solving the many-body problem. ...
en.wikipedia.org/wiki/Quantum_Monte_Carlo - 32k - Cached - Similar pages - Note this

Quantum Monte Carlo
Uses the Hirsch-Fye algorithm, implements methods in the paper "Dynamical Mean-Field Theory of Strongly Correlated Fermion Systems".
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The Molecular Monte Carlo Home Page
"quantum" Monte Carlo, or QMC (random walks are used to compute quantum-mechanical energies and wavefunctions, often to solve electronic structure problems, ...
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Cached - Similar pages - Note this
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Simulations. Eric Roddick, David Stroud (The Ohio State University) ...
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Supersolid phases in underdamped Josephson arrays: Quantum Monte Carlo simulations.
Authors: Roddick, Eric; Stroud, David. Affiliation: ...
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Fate of Vacancy-Induced Supersolidity in $^4\text{He}$

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(Received 2 June 2006; published 22 August 2006)

The supersolid state of matter, exhibiting nondissipative flow in solids, has been elusive for 35 years. The recent discovery of a nonclassical moment of inertia in solid $^4\text{He}$ by Kim and Chan provided the first experimental evidence, although the interpretation in terms of supersolidity of the ideal crystal phase remains a subject to debate. Using quantum Monte Carlo methods we investigate the long-standing question of vacancy-induced superflow and find that vacancies in a $^4\text{He}$ crystal phase separate instead of forming a supersolid. On the other hand, nonequilibrium vacancies relaxing on defects of polycrystalline samples could provide an explanation for the experimental observations.

The observation of a nonclassical moment of inertia in solid $^4\text{He}$ by Kim and Chan (KC) has provided the first experimental evidence of a possible supersolid phase of matter [1,2], which is characterized by crystalline order and frictionless flow. Early theories of supersolidity were based on the assumption that the low-temperature $^4\text{He}$ crystal may be incommensurate (the number of atoms is not an integer multiple of that of lattice sites). As a consequence, temperatures below 0.2 K of the KC experiment. X-ray measurements [13] on hcp $^4\text{He}$ put the tightest upper bound on the vacancy concentration $n_v(T \rightarrow 0)$, disfavoring the ALC and DMI/ABH scenarios, although ABH debate the interpretation of these measurements [6]. On the theoretical side, two of us have proven that a superfluid
Why is the electron correlation important in biomolecules?

DNA Base Pair Stacking

HF or DFT cannot describe the weak attraction due to van der Waals (dispersion) interaction appropriately.

As for FMO-MP2 description for vdW interaction, see (K. Fukuzawa et al., J. Comput. Chem. 27 (2006) 948.)
Fragment Molecular Orbital Method

Divide a molecule into fragments

- N pieces of fragments (monomers)
- \([N(N-1)/2]\) pieces of fragment pairs (dimers)

FMO Total Energy

\[
E = \sum_1^N E_I + \sum_{I<J} (E_{IJ} - E_I - E_J)
\]

\[
H_I \Psi_I = E_I \Psi_I
\]

\[
H_{IJ} \Psi_{IJ} = E_{IJ} \Psi_{IJ}
\]
Examples of FMO calculation

Carbon Fixation Enzyme “Rubisco”
FMO-HF/STO-3G
Enzyme (467 amino acid residues) + Substrate
7269 atoms, 22057 AOs
Calculation time: only 5 hours
Opteron (2.0GHz) x 32 CPUs
(MP2/6-31G within 1 week)

Test Calculation

Glycine trimer

Fragment 1

Fragment 2

Fragment 3

HF-SCF calculation: ABINIT-MP
VMC calculation: CASINO code
(the Cambridge quantum Monte Carlo code)
Basis set: STO-3G

Structure Optimization
Gaussian98 (HF/STO-3G)

Study underway

DNA Base Pair Stacking

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Stacking Energy (kcal/mol)</th>
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<tbody>
<tr>
<td></td>
<td>STO–3G</td>
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</table>

- STO–3G
- 6–31G
- 3–21G
- 6–31G*

Graph showing the stacking energy as a function of distance for various basis sets.

DNA Base Pair Stacking Diagram

- Cytosine
- Guanine

Molecular models of DNA base pairs showing stacking interactions.