Quantum Cluster Methods

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Übungsaufgabe

gegeben

$N_e$ Elektronen, $N_i$ Atomkerne der Masse $M_\alpha$ und Kernladungszahl $Z_\alpha$,
lösen Sie:

$$H = -\frac{\hbar^2}{2m} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{\alpha=1}^{N_i} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_i} \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \frac{1}{4\pi\varepsilon_0} \sum_{j<k} e^2 |r_j - r_k| + \frac{1}{4\pi\varepsilon_0} \sum_{\alpha<\beta} Z_\alpha Z_\beta e^2 |R_\alpha - R_\beta|$$

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are 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.

P.M.A Dirac, *Proceedings of the Royal Society* A123, 714 (1929)
The Theory of Everything

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Contributed by David Pines, November 18, 1999

We discuss recent developments in our understanding of matter, broadly construed, and their implications for contemporary research in fundamental physics.

The Theory of Everything is a term for the ultimate theory of the universe—a set of equations capable of describing all phenomena that have been observed, or that will ever be observed (1). It is the modern incarnation of the reductionist ideal of the ancient Greeks, an approach to the natural world that has been fabulously successful in bettering the lot of mankind and continues in many people’s minds to be the central paradigm of physics. A special case of this idea, and also a beautiful instance of it, is the equation of conventional nonrelativistic quantum mechanics, which describes the everyday world of human beings—air, water, rocks, fire, people, and so forth. The details of this equation are less important than the fact that it can be written down simply and is completely specified by a handful of known quantities: the charge and mass of the electron, the charges and masses of the atomic nuclei, and Planck’s constant. For experts we write

\[ i\hbar \frac{\partial}{\partial t}|\Psi > = \mathcal{H}|\Psi > \]  

[1]

where

\[ \mathcal{H} = - \sum_{j} \frac{\hbar^2}{2m} \nabla_j^2 - \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_{j} \sum_{\alpha} Z_{\alpha} e^2 \frac{1}{|\vec{r}_j - \vec{R}_{\alpha}|} + \sum_{j<k} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} + \sum_{\alpha<\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{r}_{\beta}|}. \]  

[2]

The publication costs of this article were defrayed in part by page charge payment. This advertisement appears in these equations may be measured accurately in laboratory experiments involving large numbers of particles. The electron charge, for example, may be accurately measured by passing current through an electrochemical cell, plating out metal atoms, and measuring the mass deposited, the separation of the atoms in the crystal being known from x-ray diffraction (11). Simple electrical measurements performed on superconducting rings determine to high accuracy the quantity the quantum of magnetic flux $\hbar c/2e$ (11). A version we have learned why atoms have the size they do, why chemical bonds have the length and strength they do, why solid matter has the elastic properties it does, why some things are transparent while others reflect or absorb light (6). With a little more experimental input for guidance it is even possible to predict atomic conformations of small molecules, simple chemical reaction rates, structural phase transitions, ferromagnetism, and sometimes even superconducting transition temperatures (7). But the schemes for approximating are not first-principles deductions but are rather art keyed to experiment, and thus tend to be the least reliable precisely when reliability is most needed, i.e., when experimental information is scarce, the physical behavior has no precedent, and the key questions have not yet been identified. There are many notorious failures of alleged ab initio computation methods, including the phase diagram of liquid $^3$He and the entire phenomenology of high-temperature superconductors (8–10). Predicting protein functionality or the behavior of the human brain from these equations is patently absurd. So the triumph of the reductionism of the Greeks is a pyrrhic victory: We have succeeded in reducing all of ordinary physical behavior to a simple, correct Theory of Everything only to discover that it has revealed exactly nothing about many things of great importance.

In light of this fact it strikes a thinking person as odd that the parameters $e$, $\hbar$, and $m$ appearing in these equations may be measured accurately in laboratory experiments involving large numbers of particles. The electron charge, for example, may be accurately measured by passing current through an electrochemical cell, plating out metal atoms, and measuring the mass deposited, the separation of the atoms in the crystal being known from x-ray diffraction (11). Simple electrical measurements performed on superconducting rings determine to high accuracy the quantity the quantum of magnetic flux $\hbar c/2e$ (11). A version
what atoms to pick?
what materials are interesting?
electronic Hamiltonian in Born-Oppenheimer approximation

\[
H = -\frac{1}{2} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_i} \frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e} \frac{1}{|r_j - r_k|} + \sum_{\alpha<\beta}^{N_i} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}
\]

given a material \{Z_\alpha, R_\alpha\}

solve

\[
H\Psi(x_1, \ldots, x_N) = E\Psi(x_1, \ldots, x_N)
\]

antisymmetrize wavefunction
antisymmetric wave-functions

(anti)symmetrization of $N$-body wave-function: $N!$ operations

$$S_{\pm} \psi(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P \psi(x_{p(1)}, \ldots, x_{p(N)})$$

antisymmetrization of products of single-particle states

$$S_{-} \varphi_{\alpha_1}(x_1) \cdots \varphi_{\alpha_N}(x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

much more efficient: scales only polynomially in $N$

Slater determinant: $\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)$
Slater determinants

$$\Phi_{\alpha_1 \ldots \alpha_N}(x) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

simple examples

$N=1$: $$\Phi_{\alpha_1}(x_1) = \varphi_{\alpha_1}(x_1)$$

$N=2$: $$\Phi_{\alpha_1\alpha_2}(x_1, x_2) = \frac{1}{\sqrt{2}} \left( \varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2) \right)$$

expectation values need only one antisymmetrized wave-function:

$$\int dx \ (S_{\pm}\psi_a(x)) \ M(x) \ (S_{\pm}\psi_b(x)) = \int dx \left( \sqrt{N!} \psi_a(x) \right) \ M(x) \ (S_{\pm}\psi_b(x))$$

remember: $M(x_1, \ldots, x_N)$ symmetric in arguments

corollary: overlap of Slater determinants:

$$\int dx_1 \cdots dx_N \ \Phi_{\alpha_1 \ldots \alpha_N}(x_1, \ldots, x_N) \Phi_{\beta_1 \ldots \beta_N}(x_1, \ldots, x_N) = \det \left( \langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \right)$$
basis of Slater determinants

\[
\int dx_1 \cdots dx_N \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det \left( \langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \right)
\]

Slater determinants of ortho-normal orbitals \( \varphi_\alpha(x) \) are normalized

a Slater determinant with two identical orbital indices vanishes (Pauli principle)

Slater determinants that only differ in the order of the orbital indices are (up to a sign) identical

define **convention for ordering indices**, e.g. \( \alpha_1 < \alpha_2 < \cdots < \alpha_N \)

given \( K \) (ortho-normal orbitals) \( \{ \varphi_\alpha(x) \mid \alpha \in \{1, \ldots, K\} \} \)

the \( K! / N! (K-N)! \) Slater determinants

\[
\left\{ \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \right\vert \alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1, \ldots, K\} \}
\]

are an (ortho-normal) basis of the \( N \)-electron Hilbert space
second quantization: motivation

keeping track of all these signs...

Slater determinant

$$\Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} (\varphi_\alpha(x_1)\varphi_\beta(x_2) - \varphi_\beta(x_1)\varphi_\alpha(x_2))$$

corresponding Dirac state

$$|\alpha, \beta\rangle = \frac{1}{\sqrt{2}} (|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle)$$

use operators

$$|\alpha, \beta\rangle = c_\beta^\dagger c_\alpha^\dagger |0\rangle$$

position of operators encodes signs

$$c_\beta^\dagger c_\alpha^\dagger |0\rangle = |\alpha, \beta\rangle = -|\beta, \alpha\rangle = -c_\alpha^\dagger c_\beta^\dagger |0\rangle$$

product of operators changes sign when commuted: anti-commutation

anti-commutator

$$\{A, B\} := AB + BA$$
second quantization: motivation

specify $N$-electron states using operators

$N=0$:  $|0\rangle$ (vacuum state)

normalization:  $\langle0|0\rangle = 1$

$N=1$:  $|\alpha\rangle = c^\dagger_\alpha|0\rangle$ (creation operator adds one electron)

normalization:  $\langle\alpha|\alpha\rangle = \langle0|c_\alpha c^\dagger_\alpha|0\rangle$

overlap:  $\langle\alpha|\beta\rangle = \langle0|c_\alpha c^\dagger_\beta|0\rangle$

adjoint of creation operator removes one electron:

annihilation operator

$c_\alpha|0\rangle = 0$ and $c_\alpha c^\dagger_\beta = \pm c^\dagger_\beta c_\alpha + \langle\alpha|\beta\rangle$

$N=2$:  $|\alpha,\beta\rangle = c^\dagger_\beta c^\dagger_\alpha|0\rangle$

antisymmetry:  $c^\dagger_\alpha c^\dagger_\beta = -c^\dagger_\beta c^\dagger_\alpha$
second quantization: formalism

vacuum state $|0\rangle$
and
set of operators $c_\alpha$ related to single-electron states $\varphi_\alpha(x)$ defined by:

\[
\begin{align*}
c_\alpha |0\rangle &= 0 \\
\langle 0|0 \rangle &= 1
\end{align*}
\]

\[
\{ c_\alpha, c_\beta \} = 0 = \{ c_\alpha^\dagger, c_\beta^\dagger \}
\]

\[
\{ c_\alpha, c_\beta^\dagger \} = \langle \alpha|\beta \rangle
\]

see also
www.cond-mat.de/events/correl13/manuscripts/koch.pdf
second quantization: field operators

creation/annihilation operators in real-space basis

\[ \hat{\Psi}^\dagger(x) \text{ with } x = (r, \sigma) \text{ creates electron of spin } \sigma \text{ at position } r \]

then \[ c_{\alpha}^\dagger = \int dx \varphi_{\alpha}(x) \hat{\Psi}^\dagger(x) \]

\( \{ \varphi_{\alpha_n}(x) \} \) complete orthonormal set

\[ \sum_j \overline{\varphi_{\alpha_j}(x)} \varphi_{\alpha_j}(x') = \delta(x - x') \]

\[ \hat{\Psi}(x) = \sum_n \varphi_{\alpha_n}(x) c_{\alpha_n} \]

they fulfill the standard anti-commutation relations

\[ \{ \hat{\Psi}(x), \hat{\Psi}(x') \} = 0 = \{ \hat{\Psi}^\dagger(x), \hat{\Psi}^\dagger(x') \} \]

\[ \{ \hat{\Psi}(x), \hat{\Psi}^\dagger(x') \} = \delta(x - x') \]
second quantization: Slater determinants

\[\Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \langle 0 \mid \hat{\psi}(x_1) \hat{\psi}(x_2) \ldots \hat{\psi}(x_N) c_{\alpha_N}^\dagger \ldots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \mid 0 \rangle\]

proof by induction

\(N=0: \quad \Phi() = \langle 0|0\rangle = 1\)

\(N=1: \quad \langle 0 \mid \hat{\psi}(x_1) c_{\alpha_1}^\dagger \mid 0 \rangle = \langle 0 \mid \varphi_{\alpha_1}(x_1) - c_{\alpha_1}^\dagger \hat{\psi}(x_1) \mid 0 \rangle = \varphi_{\alpha_1}(x_1)\)

using \(\{\hat{\psi}(x), c_{\alpha}^\dagger\} = \int dx' \varphi_{\alpha}(x') \{\hat{\psi}(x), \hat{\psi}^\dagger(x')\} = \varphi_{\alpha}(x)\)

\(N=2: \quad \langle 0 \mid \hat{\psi}(x_1) \hat{\psi}(x_2) c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \mid 0 \rangle\)

\[= \langle 0 \mid \hat{\psi}(x_1) (\varphi_{\alpha_2}(x_2) - c_{\alpha_2}^\dagger \hat{\psi}(x_2)) c_{\alpha_1}^\dagger \mid 0 \rangle\]

\[= \langle 0 \mid \hat{\psi}(x_1) c_{\alpha_1}^\dagger \mid 0 \rangle \varphi_{\alpha_2}(x_2) - \langle 0 \mid \hat{\psi}(x_1) c_{\alpha_2}^\dagger \hat{\psi}(x_2) c_{\alpha_1}^\dagger \mid 0 \rangle\]

\[= \varphi_{\alpha_1}(x_1) \varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1) \varphi_{\alpha_1}(x_2)\]
second quantization: Slater determinants

general $N$: commute $\Psi(x_N)$ to the right

$$
\langle 0 | \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \hat{\psi}(x_N) \ c_{\alpha_N}^\dagger \ c_{\alpha_{N-1}}^\dagger \ldots \ c_{\alpha_1}^\dagger | 0 \rangle = 
$$

$$
+ \langle 0 | \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \ c_{\alpha_{N-1}}^\dagger \ldots \ c_{\alpha_1}^\dagger | 0 \rangle \varphi_{\alpha_N}(x_N)
$$

$$
- \langle 0 | \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \ \prod_{n\neq N-1} c_{\alpha_n}^\dagger | 0 \rangle \varphi_{\alpha_{N-1}}(x_N)
$$

$$
\vdots
$$

$$
(-1)^N \langle 0 | \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \ c_{\alpha_N}^\dagger \ldots \ c_{\alpha_2}^\dagger | 0 \rangle \varphi_{\alpha_1}(x_N)
$$

Laplace expansion in terms of $N-1$ dim determinants wrt last row of

$$
= 
\begin{vmatrix}
\varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \ldots & \varphi_{\alpha_N}(x_1) \\
\varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \ldots & \varphi_{\alpha_N}(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \ldots & \varphi_{\alpha_N}(x_N) \\
\end{vmatrix}
$$
second quantization: Dirac notation

Product state \( c_{\alpha_N}^\dagger \cdots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \ket{0} \)

corresponds to

Slater determinant \( \Phi_{\alpha_1 \alpha_2 \ldots \alpha_N} (x_1, x_2, \ldots, x_N) \)

as

Dirac state \( \ket{\alpha} \)

corresponds to

wave-function \( \varphi_\alpha (x) \)
second quantization: expectation values

expectation value of $N$-body operator wrt $N$-electron Slater determinants

$$
\int dx_1 \cdots dx_N \Phi_{\beta_1 \cdots \beta_N}(x_1, \cdots, x_N) M(x_1, \cdots, x_N) \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \cdots, x_N) = \left\langle 0 \right| c_{\beta_1} \cdots c_{\beta_N} \hat{M} c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \left| 0 \rightangle
$$

$$
\int dx_1 \cdots dx_N \frac{1}{\sqrt{N!}} \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \right| 0 \rightangle M(x_1, \cdots, x_N) \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \right| 0 \rightangle
$$

$$
= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \frac{1}{N!} \int dx_1 \cdots dx_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) M(x_1, \cdots, x_N) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \right| 0 \rightangle
$$

$$
|0\rangle\langle 0| = 1 \text{ on 0-electron space}
$$

collecting field-operators to obtain $M$ in second quantization:

$$
\hat{M} = \frac{1}{N!} \int dx_1 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) M(x_1, \cdots, x_N) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)
$$

apparently dependent on number $N$ of electrons!
second quantization: zero-body operator

zero-body operator $M_0(x_1,...x_N)=1$ independent of particle coordinates

second quantized form for operating on $N$-electron states:

$$\hat{M}_0 = \frac{1}{N!} \int dx_1 dx_2 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_2) \hat{\psi}^\dagger(x_1) \hat{\psi}(x_1) \hat{\psi}(x_2) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \int dx_2 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_2) \hat{\n}\hat{\psi}(x_2) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \int dx_2 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_2) 1 \hat{\psi}(x_2) \cdots \hat{\psi}(x_N)$$

$$\vdots$$

$$= \frac{1}{N!} 1 \cdot 2 \cdots N = 1$$

only(!) when operating on $N$-electron state using $$\int dx \hat{\psi}^\dagger(x)\hat{\psi}(x) = \hat{N}$$

result independent of $N$
Second quantization: one-body operators

One-body operator

\[ M(x_1, \ldots, x_N) = \sum_j M_1(x_j) \]

\[ \hat{M}_1 = \frac{1}{N!} \int dx_1 \cdots dx_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_j M_1(x_j) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) \]

\[ = \frac{1}{N!} \sum_j \int dx_j \hat{\psi}^\dagger(x_j) M_1(x_j) (N - 1)! \hat{\psi}(x_j) \]

\[ = \frac{1}{N} \sum_j \int dx_j \hat{\psi}^\dagger(x_j) M_1(x_j) \hat{\psi}(x_j) \]

\[ = \int dx \ \hat{\psi}^\dagger(x) M_1(x) \hat{\psi}(x) \]

Result independent of \( N \)

Expand in complete orthonormal set of orbitals

\[ \hat{M}_1 = \sum_{n,m} \int dx \ \varphi_{\alpha_n}(x) M(x) \varphi_{\alpha_m}(x) \ c_{\alpha_n}^\dagger c_{\alpha_m} = \sum_{n,m} \langle \alpha_n | M_1 | \alpha_m \rangle \ c_{\alpha_n}^\dagger c_{\alpha_m} \]
second quantization: two-body operators

two-body operator

$$M(x_1, \ldots, x_N) = \sum_{i<j} M_2(x_i, x_j)$$

$$\hat{M}_2 = \frac{1}{N!} \int dx_1 \cdots dx_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_{i<j} M_2(x_i, x_j) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \sum_{i<j} \int dx_i dx_j \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) M_2(x_i, x_j) (N - 2)! \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{N(N - 1)} \sum_{i<j} \int dx_i dx_j \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) M_2(x_i, x_j) \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{2} \int dx \, dx' \, \hat{\psi}^\dagger(x') \hat{\psi}^\dagger(x) M_2(x, x') \hat{\psi}(x) \hat{\psi}(x')$$

result independent of $N$

expand in complete orthonormal set of orbitals

$$\hat{M}_2 = \frac{1}{2} \sum_{n,n',m,m'} \int dx \, dx' \, \varphi_{\alpha_n'}(x') \varphi_{\alpha_n}(x) M_2(x, x') \varphi_{\alpha_m}(x) \varphi_{\alpha_{m'}}(x') c_{\alpha_n'}^\dagger c_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

$$= \frac{1}{2} \sum_{n,n',m,m'} \langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle \ c_{\alpha_n'}^\dagger c_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$
**BO Hamiltonian**

Electronic Hamiltonian in Born-Oppenheimer approximation

\[
H = -\frac{1}{2} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_i} \frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k} \frac{1}{|r_j - r_k|} + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}
\]

solve \( H|\Psi(x_1, \ldots, x_N) = E|\Psi(x_1, \ldots, x_N) \) and antisymmetrize

solve \( H|N_e\rangle = E|N_e\rangle \), where

\[
H = -\sum_{\alpha\beta} t_{\alpha\beta} c_\alpha^\dagger c_\beta + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} U_{\alpha\delta}^{\beta\gamma} \ c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta \n |N_e\rangle = \sum a_{\alpha_1, \ldots, \alpha_{N_e}} \ \prod_i c_i^\dagger |0\rangle
\]

\[
t_{\alpha\beta} = \sum_{\alpha'\beta'} (S^{-1})_{\alpha\alpha'} \int dx \ \overline{\varphi_{\alpha'}(x)} \left( \frac{1}{2} \nabla^2 - V_{\text{ext}}(\vec{r}) \right) \varphi_{\beta'}(x) \ (S^{-1})_{\beta'\beta}
\]

\[
U_{\alpha\delta}^{\beta\gamma} = \sum_{\alpha''\beta''\gamma''} \frac{1}{S_{\alpha\alpha'}^{-1} S_{\beta\beta'}^{-1}} \int dx \int dx' \ \overline{\varphi_{\alpha'}(x)} \varphi_{\beta'}(x') \frac{1}{|\vec{r} - \vec{r}'|} \varphi_{\gamma'}(x') \varphi_{\delta'}(x) \ S^{-1}_{\gamma'\gamma} S^{-1}_{\delta'\delta}
\]
approximation: restrict basis set

formulations in 1\textsuperscript{st} and 2\textsuperscript{nd} quantization equivalent, as long as basis set complete

restrict basis set to $K$ functions $\varphi_\alpha$

$N$-electron Hilbert space restricted to binom($K,N$)-dimensional \textit{variational} space

all-electron approach:
increase $K$ until convergence

pseudized approach:
variational space only for \textit{interesting} electrons

how?
perturbation theory
renormalization
H_1 should be small perturbation

U_{scf} must describe electron-electron repulsion well

accurate density gives accurate Hartree term

DFT orbitals!

open shell – degenerate perturbation theory
Q. Zhang: 
Calculations of Atomic Multiplets across the Periodic Table 
MSc thesis, RWTH Aachen 2014 
www.cond-mat.de/sims/multiplet
Hund’s rule: $d^5$ ground state $^6S$

\[ |0, 0, 5/2, 5/2\rangle = c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \]

\[ |0, 0, 5/2, 3/2\rangle = \frac{1}{\sqrt{5}} \left( c_{2\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{1\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{0\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-1\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

\[ |0, 0, 5/2, 1/2\rangle = \frac{1}{\sqrt{10}} \left( c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

\[ |0, 0, 5/2, -1/2\rangle = \frac{1}{\sqrt{10}} \left( c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

\[ |0, 0, 5/2, -3/2\rangle = \frac{1}{\sqrt{5}} \left( c_{-1\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-2\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-2\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger - c_{-2\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger + c_{-2\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

\[ |0, 0, 5/2, -5/2\rangle = c_{-2\downarrow}^\dagger c_{-1\downarrow}^\dagger c_{0\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\downarrow}^\dagger |0\rangle \]

\[ E_{^6S} = 10 F^{(0)} - \frac{5}{7} \left( F^{(2)} + F^{(4)} \right) \]

Slater integrals \( F_{nl}^{(k)} = \int_0^\infty dr |u_{nl}(r)|^2 \left( \frac{1}{r^{k+1}} \int_0^r d\tilde{r} \tilde{r}^k |u_{nl}(\tilde{r})|^2 + r^k \int_r^\infty d\tilde{r} \frac{1}{\tilde{r}^{k+1}} |u_{nl}(\tilde{r})|^2 \right) \)

Spin-Orbit coupling \( H_{SO} = \frac{1}{2c^2} \sum_i \frac{1}{r_i} \frac{dV}{dr_i} \ell_i \cdot s_i \)
LS coupling: Co$^{4+}$
LS coupling: $\text{Co}^{4+}$

Configuration | Coulomb repulsion | Spin-orbit | $\text{Hu}+\text{Hso}$
--- | --- | --- | ---
$6S$ | 9.914828 | | $6S(5/2)$ | 9.914828

$6S$ character
non-LS coupling: Ir$^{4+}$
non-LS coupling: Ir$^{4+}$
non-LS coupling: Ir atom
modeling correlated electrons: renormalization

\[ H = -\frac{1}{2} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_i} \frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e} \frac{1}{|r_j - r_k|} \]

complete orbital basis \( \phi_{n,i} \quad H = - \sum_{n,i;m,j;\sigma} t_{n,i;m,j} a_\sigma^\dagger m,j a_{n,i} + \sum_i V_{n,i\sigma;m,j\sigma'} n_{n,i\sigma} n_{m,j\sigma'} \)

distinguish two types of electrons/orbitals: correlated and uncorrelated
assume no hybridization between them: product ansatz

\[ \psi(\{n_{n,i\sigma}\}) = \sum_n \sum_\mu \alpha_{i,\mu} \psi_n(\{n_{c,i\sigma}\}) \Phi_\mu(\{n_{c,i\sigma}\}; \{n_{a,j\sigma'}\}) \approx \psi_0 \Phi(\{n_{c,i\sigma}\}) \]

instant-screening approx.: slow correlated, fast other electrons

\[ H|\psi\rangle = E|\psi\rangle \Rightarrow \langle \Phi|H|\Phi\rangle|\psi\rangle = E|\psi\rangle \]
simple example: 3-band Hubbard cluster

\[ U_{11} = 1.5 \]
\[ U_{22} = 0.6 \]
\[ U_{33} = 0.2 \]
\[ U_{12} = 0.7 \]
\[ U_{23} = 0.05 \]
\[ t_{22} = 0.1 \]
\[ t_{13} = 0.5 \]
\[ \Delta = 0.5 \]
spectral function: projected vs. 1-band
screening $U$

instantaneous screening approximation

$0 \quad \varepsilon \quad 2\varepsilon + U$

$N = 2 \quad N = 3 \quad N = 4$
spectral function: projected vs. 1-band

\[ G_{22} \]

1-band \( U_{\text{bare}, \ t_{\text{bare}}} \)
1-band \( U_{\text{eff}, \ t_{\text{bare}}} \)
1-band \( U_{\text{eff}, \ t_{\text{inst}}} \)
overlap between different screening states reduces hopping: $t_{\text{eff}}$
spectral function: projected vs. 1-band
screening reduces $U$ and $t$

could justify that constrained calculations tend to give “too small $U$”

$t/U$ not as sensitive to screening as one might think

C. Adolphs: Renormalization of the Coulomb Interaction in the Hubbard Model
Diploma Thesis, RWTH Aachen 2010
surface effects

10×10×10 cluster

$8^3 = 2^9 = 512$ atoms inside

almost 50% of atoms on surface...

how to simulate bulk?

periodic boundary conditions
finite size scaling

half-filled one-dimensional L-site chain

\[ E_{\text{tot}}/L = -1.28 \]

\[ E_{\text{pbc}} = -2t \sum_{\sigma} \sum_{n=-[N_{\sigma}/2]}^{-[N_{\sigma}/2]+N_{\sigma}} \cos(2\pi n/L) \]

\[ E_{\text{obc}} = -2t \sum_{\sigma} \sum_{n=1}^{N_{\sigma}} \cos(2\pi n/(L + 1)) \]
periodic boundary conditions

additional interaction with periodic images

\[ H_{\text{pbc}} = -\frac{1}{2} \sum_{i=1}^{N} \vec{\nabla}_{i}^{2} + \sum_{\vec{n} \in \mathbb{Z}^{3}} \sum_{i} V_{\text{ext}}^{c}(\vec{r}_{i} - \vec{R}_{\vec{n}}) + \frac{1}{2} \sum_{\vec{n} \in \mathbb{Z}^{3}} \sum_{i,j} ' \frac{1}{|\vec{r}_{i} - \vec{r}_{j} - \vec{R}_{\vec{n}}|} \]

finite-size correction \[ \varepsilon = \left( E_{\text{corr}}(L) - E_{\text{MF}}(L) \right) / L + \varepsilon_{\text{MF}} \]
exchange-correlation hole

electron density: $\Gamma(x; x) = n(x)$

conditional electron density: $2\Gamma(x, x'; x, x') = n(x, x')$

Coulomb repulsion

$$\langle U \rangle = \int dx \, dx' \frac{\Gamma^{(2)}(x, x'; x, x')}{|r - r'|} = \frac{1}{2} \int dx \, dx' \frac{n(x, x')}{|r - r'|}$$

rewrite in terms of Hartree energy

(how $\langle U \rangle$ differs from mean-field)

$$n(x, x') = n(x)n(x') \, g(x, x') = n(x)n(x') + n(x)n(x') \, (g(x, x') - 1)$$

pair correlation function

Hartree term

exchange-correlation hole

sum rule

$$\int dx' \, n(x, x') = n(x) (N - 1)$$

$$\int dx' \, n(x') \, (g(x, x') - 1) = -1$$
exchange-correlation holes from QMC

homogeneous electron gas

\[ g_{xc}^{\sigma\sigma'}(r / r_s) \]

G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)

(110) plane of Si, electron at bond center

\[ g_{xc}^{\text{VMC}}(\vec{r}) \]

lattices

\[ \mathcal{L}_A = \left\{ \sum_i n_i a_i \mid n_i \in \mathbb{Z} \right\} \]

primitive lattice vectors

\[ A = (a_1, a_2, \ldots, a_d) \]

not unique

canonical choice:
 vectors to nearest neighbors
 (LLL algorithm)

allowed transformations of \( A \):
• exchange vectors
• change sign of vector
• add int multiple of other vector

\[ \mathcal{L}_A = \left\{ A n \mid n \in \mathbb{Z}^d \right\} \]

\[ V_c = |\det(A)| \]
\[ d \to \infty \text{ applications to cryptography} \]
lattice periodic functions

Fourier transform

\[ V(\mathbf{r}) = \int d\mathbf{k} \hat{V}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \]

lattice periodicity

\[ V(\mathbf{r} + A\mathbf{n}) = \int d\mathbf{k} \hat{V}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} e^{i\mathbf{k} \cdot A\mathbf{n}} = V(\mathbf{r}) = 1 \]

only modes that contribute

\[ \mathbf{k} \in \left\{ \mathbf{G} \mathbf{m} \mid \mathbf{m} \in \mathbb{Z}^d \right\} = \mathcal{R}_\mathcal{L} \quad \text{with} \quad \mathbf{G} = (2\pi \mathbf{A}^{-1})^T \]

\[ \mathbf{G} \mathbf{m} \cdot A \mathbf{n} = \mathbf{m}^T \mathbf{G}^T A \mathbf{n} = 2\pi \times \text{integer} \]

\[ 2\pi \]
Bloch theorem

lattice-periodic potential

\[ H_{\text{single}} = \sum_k \frac{k^2}{2} c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_k \sum_{m \in \mathbb{Z}^d} \hat{V}_m c_{k+G_m,\sigma}^\dagger c_{k,\sigma} \]

eigenstates: Bloch waves

\[ \varphi_{n,k}(r) = \sum_{m \in \mathbb{Z}^d} c_{n,m} e^{i(k+G_m) \cdot r} \sim \varphi_{n,k}(r + An) = e^{ik \cdot An} \varphi_{n,k}(r) \]

reduce eigenvalue problem to single unit cell with pbc

\[ \left( \frac{1}{2} \left( -i \nabla_r + k \right)^2 + V(r) \right) u_{n,k}(r) = \varepsilon_{n,k} u_{n,k}(r) \]

vector potential

\[ \varphi_{n,k}(r) = e^{ik \cdot r} u_{n,k}(r) \]
many-electron Bloch theorem

\[ H = \sum_{k,\sigma} \left( \frac{k^2}{2} c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_m \hat{V}_{Gm} c_{k+Gm,\sigma}^\dagger c_{k,\sigma} + \frac{1}{2} \sum_{k',\sigma';q} c_{k+q,\sigma}^\dagger c_{k'-q,\sigma'}^\dagger \frac{1}{|q|^2} c_{k',\sigma'} c_{k,\sigma} \right) \]

couples all states with given total crystal momentum (invariance under translation of all electrons by lattice vector)

to move all electrons into a simulation cell \( C \), need to postulate Bloch-like theorem

\[ \psi^C_{n,\tilde{k}}(r_1, r_2, \ldots) = e^{i\tilde{k} \cdot \sum_i r_i} U^C_{n,\tilde{k}}(r_1, r_2, \ldots) \]

\( k \) enters eigenvalue equation for \( U^C \) as a vector potential

susceptibility \[ \left. \frac{d^2 E(k)}{dk^2} \right|_{k=0} \]
distinguish metals from (Mott) insulators

Kohn, Phys. Rev. 133, A171 (1964)
supercells

\[ C = A L \quad V = |\det(C)| \]
Hermite normal form

\[ \Lambda = \begin{pmatrix} \lambda_{11} & 0 & 0 & \cdots \\ \lambda_{21} & \lambda_{22} & 0 \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \\ \vdots & \vdots & \ddots \end{pmatrix} \quad 0 \leq \lambda_{ij} < \lambda_{ii} \]

Euclidean algorithm

\[ \gcd(a, b) = \begin{cases} |a| & \text{if } b = 0 \quad \text{(change sign of column)} \\ \gcd(b, a) & \text{if } |a| < |b| \quad \text{(exchange columns)} \\ \gcd(a - \lfloor a/b \rfloor b, b) & \text{otherwise} \quad \text{(add integer multiple of col)} \end{cases} \]
Hermite normal form

\[ \mathbf{L} : \left( \begin{array}{cc} 2 & 0 \\ 4 & 8 \end{array} \right)_{\text{HNF}} \left( \begin{array}{cc} 4 & 2 \\ 0 & 4 \end{array} \right) \left( \begin{array}{cc} 0 & 4 \\ -4 & -2 \end{array} \right) \left( \begin{array}{cc} 4 & 8 \\ -2 & 0 \end{array} \right) \left( \begin{array}{cc} 4 & 0 \\ 2 & 4 \end{array} \right)_{\text{HNF}} \]
supercell: \( k \)-point sampling

\[
K_S = (2\pi C^{-1})^T = G(L^{-1})^T
\]
supercell: $k$-point sampling

$$K_S = (2\pi C^{-1})^T = G(L^{-1})^T$$
Monkhorst-Pack grid

particularly suited for Brillouin-zone integrals

\[ L = \begin{pmatrix} n_1 & 0 & 0 \\ 0 & n_2 & 0 \\ 0 & 0 & n_3 \end{pmatrix} \]

\[ \tilde{k} = \sum_i \frac{(n_i - 1)k_i}{2n_i} \]

Special points for Brillouin-zone integrations*

Hendrik J. Monkhorst and James D. Pack

Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 21 January 1976)

A method is given for generating sets of special points in the Brillouin zone which provides an efficient means of integrating periodic functions of the wave vector. The integration can be over the entire Brillouin zone or over specified portions thereof. This method also has applications in spectral and density-of-state calculations. The relationships to the Chadi-Cohen and Gilat-Raubenheimer methods are indicated.
S. Redner: *Citation Statistics from 110 years of Physical Review*  
Physics Today June 2005, p. 49

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S. Redner: A Physicist’s Perspective on Citation Analysis
Trends in Research Measurement Metrics, Washington DC, Oct 2010
Conclusions

**second quantization**

\[ c_\alpha|0\rangle = 0 \quad \{ c_\alpha, c_\beta^\dagger \} = 0 = \{ c_\alpha^\dagger, c_\beta \} \]

\[ \langle 0|0\rangle = 1 \quad \{ c_\alpha, c_\beta^\dagger \} = \langle \alpha|\beta \rangle \]

\[ \Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N) \sim c_{\alpha_N}^\dagger \cdots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger |0\rangle \]

**degenerate perturbation theory**

many-body Bloch supercell &

renormalized models