Quantum Chemistry I

Mathematical Backgrounds

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List of Contents

Linear Space

In the very beginning, we have to revise some of the basic notions.

Linear Space

A linear space V on field $\mathcal{F}$ is defined as a set eqquiped with two operations: addition $V \times V \to V$ and scalar product $\mathcal{F} \times V \to V$, with the operations satisfying:

1. addition associativity: $(u + v) + w = u + (v + w) = u + v + w$
2. existance of identity element: there exists 0, $0 + v = v$
3. existance of inverse elements: for any v exists v', $v + v' = v' + v = 0$
4. scalar product associativity: $a(bv) = (ab)v = abv$
5. existance of identity element: there exists 1, $1v = v$
6. distributivity: $(a + b)v = av + bv$, $a(u + v) = au + av$

Linear Space

pre-Hilbert Space

A pre-Hilbert space $\mathcal{F}$ is a linear space eqquiped with inner product

$$<,>: \mathcal{F} \times \mathcal{F} \to \mathbb{C}$$

satisfying:

1. $< au + bv, w >= a < u, w > +b < v, w >$
2. $< u, v >=< v, u >^*$
3. $< x, x >= \|x\|^2 \geq 0$. Equality holds if and only if $x = 0$.

Hilbert Space

A Hilbert space $\mathcal{H}$ is a Cauchy-complete pre-Hilbert space.

Operators

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An operator is a mapping $\mathscr{O} : u \rightarrow v$.
The operator is linear if for any u, v:

$$\mathscr{O}(au + bv) = a\mathscr{O}u + b\mathscr{O}v$$

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Exersice A: Linear operator $\mathscr{O}$ on finite-dimentional linear space V could be represented by a $dim(V) \times dim(V)$ matrix. Why?

Dirac Bra-ket Notions

Dirac denote the vectors in Hilbert spaces as $|a\rangle$. The corresponding covector is denoted as $\langle a|$. The inner product is defined as:

$$\langle a| \, |b\rangle = \langle a|b\rangle = a^\dagger b = \sum a_i^* b_i$$

Tips: use `braket` package in LaTeX.

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Exercise B: What does $|v\rangle\langle v|$ mean? Show that for a complete set of basis $|i\rangle$:

$$\sum |i\rangle\langle i| = \mathbf{1}$$

where $\mathbf{1}$ is the identity operator.

Functional Notions

The functional notions corresponds to the wave mechanics.
The vectors are now functions $a(x)$.
The inner product are defined as follows:

$$\int_{\Omega} dx a^*(x) b(x)$$

Integrals replace summations.

$$\sum |i\rangle \langle i| = \mathbf{1}$$

$$\int dx |i\rangle \langle i| = \mathbf{1}$$

Operators, Continued

Local and Nonlocal Operators

An nonlocal operator is defined like:

$$b(x) = \int_{\Omega} dx'\, O(x, x')\, a(x')$$

An local operator is defined like:

$$b(x) = \int_{\delta(x,\epsilon)} dx'\, O(x, x')\, a(x')$$

Example of local operators: x, p, L_z, ...

Operators, Continued

Commutator and Antiommutator of Operators

$$[\mathscr{A}, \mathscr{B}] = \mathscr{A}\mathscr{B} - \mathscr{B}\mathscr{A}$$
$$\{\mathscr{A}, \mathscr{B}\} = \mathscr{A}\mathscr{B} + \mathscr{B}\mathscr{A}$$

Unitary Matrices and Hermite Matrices

Unitary matrices are defined as: $A^{-1} = A^{\dagger}$
Hermite matrices are defined as: $A^{\dagger} = A$

Operators, Continued

Adjunct (or Hermite transpose)

$$A^{\dagger} = (A^{T})^{*} = (A^{*})^{T}$$

Exercise C: For a Hermite operator(which means the matrix representation of operator is Hermite) $\mathscr{A}$, $\mathscr{A}\left|a\right\rangle = \omega_a \left|a\right\rangle$

1. Prove that ω_a is real for any a.
2. Prove that $\left\langle a|b\right\rangle = \delta_{ab}$ for any a, b

Change of Basis Using Dirac Notions

Assume we have two orthogonal normalised basis $|i\rangle$ and $|a\rangle$

$$\langle i|j\rangle = \delta_{ij} \qquad \sum |i\rangle\langle i| = \mathbf{1}$$
$$\langle \alpha|\beta\rangle = \delta_{\alpha\beta} \qquad \sum |\alpha\rangle\langle \alpha| = \mathbf{1}$$

To change the basis from $|i\rangle$ to $|a\rangle$:

$$\begin{aligned} |\alpha\rangle &= \mathbf{1}\,|\alpha\rangle \\ &= \sum |i\rangle\langle i|\alpha\rangle \\ &= \sum |i\rangle\,(\mathbf{U})_{i\alpha} \end{aligned}$$

The matrix $\mathbf{U}$ is called the transformation matrix. With similar processed we could derive:

$$|i\rangle = \sum |i\rangle\,(\mathbf{U}^\dagger)_{\alpha i}$$

Change of Basis Using Dirac Notions

The matrix representation could be transformed using the same method:

$$\mathscr{O} \to \mathbf{O} \qquad \mathbf{O}_{ij} = \langle i|\, \mathscr{O}\, |j\rangle$$
$$\mathscr{O} \to \mathbf{\Omega} \qquad \mathbf{\Omega}_{\alpha\beta} = \langle \alpha|\, \mathscr{O}\, |\beta\rangle$$

$$\begin{aligned}
\Omega_{\alpha\beta} &= \langle \alpha|\, \mathscr{O}\, |\beta\rangle \\
&= \langle \alpha|\, \mathbf{1}\mathscr{O}\mathbf{1}\, |\beta\rangle \\
&= \sum_{ij} \langle \alpha|i\rangle \langle i|\, \mathscr{O}\, |j\rangle \langle j|\beta\rangle \\
&= \sum_{ij} (\mathbf{U}^\dagger)_{\alpha i} (\mathbf{O})_{ij} (\mathbf{U})_{j\beta}
\end{aligned}$$

So matrices are connected by unitary transformations:

$$\mathbf{\Omega} = \mathbf{U}^\dagger \mathbf{O} \mathbf{U} \qquad \mathbf{O} = \mathbf{U} \mathbf{\Omega} \mathbf{U}^\dagger$$

Diagonalisation

There are multiple ways of diagonalise an Hermite matrix. Here we only present the original method.
For a given matrix $\mathbf{O}$, solving the eigenvalue equations:

$$(\mathbf{O} - \lambda\mathbf{I})\mathbf{c} = 0$$

we obtain $\{\lambda_i\}$ and $\{\mathbf{c}^i\}$, and

$$\mathbf{U} = \begin{pmatrix} \mathbf{c}^1 & \mathbf{c}^2 & \dots & \mathbf{c}^N \end{pmatrix}$$

$$\mathbf{\Omega} = \mathbf{U}^\dagger\mathbf{O}\mathbf{U} = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_N \end{pmatrix}$$

Function of Matrices

For diagonalised matrices:

$$f(\mathbf{a}) = \begin{pmatrix} f(a_1) & & & \\ & f(a_2) & & \\ & & \ddots & \\ & & & f(a_N) \end{pmatrix}$$

And for undiagonalised matrices:

$$\mathbf{U}^\dagger \mathbf{A} \mathbf{U} = \mathbf{a}$$

$$\mathbf{A} = \mathbf{U} \mathbf{a} \mathbf{U}^\dagger$$

$$f(\mathbf{A}) = \mathbf{U} f(\mathbf{a}) \mathbf{U}^\dagger$$

Schrödinger Equation

Time-dependent Schrödinger Equation(TDSE)

Time-dependent Schrödinger Equation is a eigenvalue equation:

$$\mathscr{H}\left|\Phi\right\rangle = \mathscr{E}\left|\Phi\right\rangle$$

with $\mathscr{H}$ denotes Hamiltonian and $\mathscr{E}$ denotes energy.

We shall not derive the equation here.
The Hamiltonian of molecular system:

$$\mathscr{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_A \frac{1}{2}\nabla_A^2 - \sum_{i,A}\frac{Z_A}{r_{iA}} + \sum_{i<j}\frac{Z_A}{r_{ij}} + \sum_{A<B}\frac{Z_A Z_B}{R_{AB}}$$

Schrödinger Equation

There exist a set of accurate solutions to the equation:

$$\mathscr{H} |\Phi_i\rangle = \mathscr{E}_i |\Phi_i\rangle$$

with $\mathscr{E}_0 \leq \mathscr{E}_1 \leq \dots$.

We assume the set is complete, which means any state $|\tilde{\Phi}\rangle$ could be expressed in the form

$$|\tilde{\Phi}\rangle = \sum c_i |\Phi_i\rangle$$

Variational Principle

Variational Principle

For a given state $|\Psi\rangle$:

$$\frac{\langle\Psi|\,\mathscr{H}\,|\Psi\rangle}{\langle\Psi\,|\,\Psi\rangle} \geq \mathscr{E}_0$$

The equality holds if and only if $|\Psi\rangle = |\Phi_0\rangle$

Variational Principle

Now with this result we could write:

$$|\tilde{\Phi}\rangle = \sum c_i \, |\Psi_i\rangle$$

$|\Psi_i\rangle$ is a set of known functions.
Define a new matrix $\mathbf{H}$ as:

$$(\mathbf{H})_{ij} = H_{ij} = \langle\Psi_i| \mathscr{H} \, |\Psi_i\rangle$$

Assume that the state is normalised:

$$\langle\tilde{\Phi}|\tilde{\Phi}\rangle = \sum c_i^2 = 1$$

Variational Principle

As $c_1, c_2, \ldots, c_n$ is not indenpendent, Lagrange multiplier method must be put in use here:

$$\begin{aligned}\mathcal{L}(c_1, \ldots, c_N, \lambda) &= \langle \Psi_i | \mathscr{H} | \Psi_i \rangle - \lambda(\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1) \\ &= \sum c_i c_j H_{ij} - \lambda \left(\sum c_i^2 - 1 \right)\end{aligned}$$

Minimizing $\mathcal{L}$ gives:

$$\frac{\partial \mathcal{L}}{\partial c_k} = \sum c_j H_{kj} + \sum c_i H_{ik} - 2\lambda c_k = 0$$

$\mathbf{H}$ is symmetric, so:

$$\sum H_{ik} c_k = \lambda c_k$$

$$\mathbf{Hc} = \lambda \mathbf{c}$$

Variational Principle

The equation

$$\mathbf{Hc} = \lambda \mathbf{c}$$

have N different solutions:

$$\mathbf{Hc}^\alpha = \lambda_\alpha \mathbf{c}^\alpha$$

with $\lambda_0 \leq \cdots \leq \lambda_{N-1}$. As $\mathscr{H}$ is Hermite, $\mathbf{H}$ must be Hermite too, that means:

$$(\mathbf{c}^\alpha)^\dagger \mathbf{c}^\beta = \sum c_i^\alpha c_i^\beta = \delta_{\alpha\beta}$$

Variational Principle

$$\mathbf{H}\mathbf{c}^{\alpha} = \lambda_{\alpha}\mathbf{c}^{\alpha}$$

If we define two new matrices:

$$(\mathbf{C})_{i\alpha} = C_{i\alpha} = c_i^{\alpha}$$

$$(\boldsymbol{\Lambda})_{\alpha\beta} = \Lambda_{\alpha\beta} = \lambda_{\alpha}\delta_{\alpha\beta}$$

The equation is equivalent to:

$$\mathbf{HC} = \mathbf{C}\boldsymbol{\Lambda}$$

Variational Principle

It could be proved that:

$$\lambda_\alpha = \langle\tilde{\Phi}_\alpha|\,\mathscr{H}\,|\tilde{\Phi}_\alpha\rangle$$

by combining:

$$|\tilde{\Phi}\rangle = \sum c_i\,|\Psi_i\rangle$$

$$(\mathbf{c}^\alpha)^\dagger\mathbf{c}^\beta = \sum c_i^\alpha c_i^\beta = \delta_{\alpha\beta}$$

$$\mathbf{H}\mathbf{c}^\alpha = \lambda_\alpha\mathbf{c}^\alpha$$

So we would like to denote λ as E and re-write the equations as:

$$\mathbf{HC} = \mathbf{CE}$$

Thank you for listening!