

Wavefunctions are “representations of bra and ket vectors”:

Expanding arbitrary state functions as linear combinations of the complete set of eigenfunctions of an ***observable***, dynamical variable operator **A**:

An arbitrary state vector $|f\rangle$ may be expressed as a superposition (linear combination) of members of a complete set:

$$|f\rangle = \sum_k c_{kf} |k\rangle$$

$$\hat{A}|k\rangle = a_k |k\rangle, \text{ where } a_k \text{ are the eigenvalues of } \hat{A}, \text{ and } c_{kf} = \langle k|f\rangle$$

The numbers c_{kf} are said to be: “ **$|f\rangle$ in the **A** representation”.**

One may, of course, use any other complete set to “represent” $|f\rangle$. For example, the c_{kf} from the complete set using the eigenfunctions of the Hermitian operator, d^2/dx^2 , i.e., $\sin(kx)$ and $\cos(kx)$, is the Fourier representation, better known as the **Fourier Transform**.

The set of numbers $\langle k'|B/k\rangle$ is similarly said to be the operator **B** in the **A** representation.

The Identity operator

Given that the c_{kf} are numbers = $\langle k|f\rangle$

$$|f\rangle = \sum_k c_{kf} |k\rangle = \sum_k |k\rangle c_{kf} = \sum_k |k\rangle \langle k|f\rangle$$

$$|f\rangle = \sum_k |k\rangle \langle k|f\rangle = \left(\sum_k |k\rangle \langle k| \right) |f\rangle$$

Thus, $\sum_k |k\rangle \langle k| = \hat{I}$, the very widely used “Identity” operator

Next, we introduce the special complete set known as the “position” eigenfunctions.

Position Eigenfunctions

The position operator x_{op} is simple multiplication by the position x . The eigenfunctions are *the ingenious and widely used Dirac delta functions* = $\delta(\mathbf{x}-\mathbf{a})$, where a is a real number; it has the properties:

$$\delta(x - a) = 0 \quad \text{if } x \neq a$$

$$\delta(x - a) = \infty \quad \text{if } x = a = \text{a series of infinitely high, infinitely narrow peaks.}$$

but normalized so that:

$$\int_{-\infty}^{\infty} \delta(x - a) dx = 1$$

$$\hat{x}\delta(x - a) = a\delta(x - a) \text{ i.e., } \delta(x - a) \text{ is an eigenfunction of } \hat{x} \text{ with eigenvalue } = a$$

To rationalize the normalization, one may think of the function near $x=a$ to be very large but finite in a very narrow, but finite, region such that area under the curve = 1.

Thus **expanding $|\Psi\rangle$ in the eigenfunctions of x , i.e., the Dirac delta functions, changes $|\Psi\rangle$ into the wavefunction**

$$\Psi(x) = \text{limit of } \sum_a \langle \delta(x - a) | \Psi \rangle \text{ as } x \text{ and } a \text{ become continuous.}$$

$$\Psi(x) = "|\Psi\rangle \text{ in the position representation}"$$

Wavefunctions are state kets in the position representation

Theorems

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Theorem 1. The *eigenvalues* of an Hermitian operator are real numbers

Theorem 2. The *eigenfunctions* of an Hermitian operator are orthogonal—unless the eigenvalues are degenerate. They can be made orthogonal, however

Theorem 3. A trivial result of Theorems 1 and 2.

If A is Hermitian and if g_1, g_2, \dots are a complete set of eigenfunctions of A and if $AF=kF$, then if F is expanded as:
$$F = \sum_i a_i g_i$$

the only non-zero coefficients, a_i will be for those g_i which also have eigenvalue = k

Theorem 4. If linear operators A and B have a common complete set of eigenfunctions, then A and B commute, i.e., $AB \Psi = BA \Psi$

Theorem 5. If linear operators A and B commute, then a common complete set of eigenfunctions can be constructed for them. **Example?**

For spherical systems: H , L^2 , and L_z operators all commute; thus n, l, m

and Group Theory: Symmetry operations all commute with H .

Theorem 6. If g_m and g_n are eigenfunctions of Hermitian operator A with different eigenvalues, and if the linear operator B commutes with A , then

$$\langle g_m | B | g_n \rangle = 0 \text{ for } a_n \neq a_m$$

Theorem 7. When the potential energy V is an *even* function, we can choose the stationary-state wave functions so that each Ψ_i is **either** an *even* function **or** an *odd* function

This means that H commutes with the symmetry operator called *inversion*.
Even and *odd* parity simply means eigenvalues of *inversion* = +1 or -1

Theorem 8. If $Bg_m = b_m g_m$ and $\Psi = \sum_i c_i g_i$

then if B is measured at time t when the state function is given by Ψ ,
the probability of observing the result b_m is given by $|c_m|^2$
(or the sum of $|c_m|^2$ for the degenerate states for which $c_m = b_m$.)

Theorem 9. The probability of measuring the value $b_j = \left| \langle g_j | \Psi \rangle \right|^2$

Postulates

Postulate 1. The state of a system is described by a function $\Psi(\langle \mathbf{r} \rangle, t)$, where $\langle \mathbf{r} \rangle$ stands for all $3N$ coordinates of the N particles, and t is the time. $\Psi(\langle \mathbf{r} \rangle, t)$ is called the state function or wavefunction, and contains all the information that can be determined about the system.

Ψ must be single-valued, continuous, and quadratically integrable.

For continuum states (unbound), the quadratically integrable requirement is omitted

Postulate 2. To every physically observable property there corresponds a linear Hermitian operator, where Cartesian x_{op} = multiply by x and momentum, p_x is given by

$$p_x = -i\hbar \frac{\partial}{\partial x}$$

Postulate 3. *The only possible result from a measurement of property B, corresponding to operator **B**, are the eigenvalues of **B**.*

Postulate 4. *If B is a linear Hermitian operator that represents a physical property, the eigenfunctions g_i of B form a complete set*

(This must be a postulate because it can't be proven, and there are Hermitian operators whose eigenfunctions do not form complete set!)

Postulate 5. The average (or expectation value) of a property B is given by

$$\int_{\text{all space}} \Psi^* B \Psi d\tau = \langle \Psi | B | \Psi \rangle$$

Postulate 6. The time dependent Schrodinger Equation:

$$\frac{\partial}{\partial t} \Psi = -\frac{i}{\hbar} H \Psi \quad \text{or, } i \hbar \frac{\partial}{\partial t} \Psi = H \Psi \quad \text{or, } -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi = H \Psi$$

“The” Variation Principle and Variation Methods

One cannot overemphasize the immense importance of “the” variation principle to quantum chemistry, but it is equally important in numerous other fields, many of them in non-quantum engineering applications. It turns out that eigenvalues and eigenvectors always emerge when a differential equation is subjected to boundary conditions.

Schrödinger himself invoked a variation principle to support his formulation of the Schrödinger Equation.

Quoting from https://en.wikipedia.org/wiki/Variational_principle: A **variational principle** is a scientific principle used within the [calculus of variations](#), which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. “For example...the shape of a chain suspended at both ends... is found by minimizing the gravitational potential energy”

Examples

- [Lord Rayleigh's variational principle](#)
- [Ekeland's variational principle](#)
- [Fermat's principle](#) in [geometrical optics](#)
- The [principle of least action](#) in [mechanics](#), [electromagnetic theory](#), and [quantum mechanics](#)
- [Maupertuis' principle](#) in [classical mechanics](#)
- The [Einstein equation](#) also involves a variational principle, the [Einstein–Hilbert action](#)
- [Gauss's principle of least constraint](#)
- [Hertz's principle of least curvature](#)
- [Palatini variation](#)
- The [variational method](#) in quantum mechanics
- The [finite element method](#)

The Variation Principle of Quantum Systems

$$\frac{\int \phi_{trial}^* H \phi_{trial} d\tau}{\int \phi_{trial}^* \phi_{trial} d\tau} = \langle E \rangle \geq E_0$$

The power of the variation principle is that **any** approximate wavefunction for the ground state of a quantum system is **guaranteed** to give an energy expectation value, $\langle E_{approx} \rangle$, that will be **higher than the true ground state energy, E_0** .

This allows one to vary the “shape” of the trial wavefunction by **any** means available, until the derivative of $\langle E_{approx} \rangle$ with respect to all variables being varied = 0, simultaneously, and thus be satisfied that this will be the most accurate wave function of the type being used as ϕ_{trial} .

There is no danger of finding an energy that is too low!

In addition to the above “**wavefunction**” scheme, Kohn and Sham shared the Nobel Prize recently for proving and helping implement the so **called density functional theory (DFT)**.

With **DFT**, one directly varies the electron density $\phi_{trial}^* \phi_{trial}$ to reach the energy minimum, instead of varying ϕ_{trial} , which must always be squared to get the energy anyway.

There are different variation methods which can be classified into two broad classes: (1) linear variation method, and (2) non-linear variation methods. We will begin with simple examples of the **non-linear variation method**, Then **spend much time on the linear variation method**, which pervades most of the computational methods we will encounter in chemistry.

A quick example is using the exact form of the ground state wavefunction for a hydrogen-like atom or ion.

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{r} = -\frac{1}{2} \nabla^2 - \frac{Z}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{2r^2} L^2(\theta, \varphi)$$

if we don't know that $\phi_0 = e^{-\frac{Zr}{a}} = e^{-Zr}$ in atomic units

We guess that:

$$\phi_{\text{trial}} = e^{-\frac{\alpha r}{a}} = e^{-\alpha r} \text{ in atomic units}$$

$$\frac{\int \phi_{\text{trial}}^* H \phi_{\text{trial}} d\tau}{\int \phi_{\text{trial}}^* \phi_{\text{trial}} d\tau} = \langle E \rangle$$

$$d\tau = r^2 dr \sin \theta d\phi$$

$$\langle E \rangle = \frac{\int e^{-\alpha r} H e^{-\alpha r} d\tau}{\int e^{-\alpha r} e^{-\alpha r} d\tau} = \frac{\int e^{-\alpha r} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{Z}{r} \right) e^{-\alpha r} 4\pi^2 r^2 dr}{\int e^{-2\alpha r} 4\pi^2 r^2 dr}$$

$$\langle E \rangle = \frac{\int e^{-\alpha r} H e^{-\alpha r} d\tau}{\int e^{-\alpha r} e^{-\alpha r} d\tau} = \frac{\int e^{-\alpha r} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{Z}{r} \right) e^{-\alpha r} 4\pi^2 r^2 dr}{\int e^{-2\alpha r} 4\pi^2 r^2 dr}$$

$$\int_0^{\infty} r^n e^{-br} dr = \frac{n!}{b^{n+1}}$$

$$\text{For } n = 1 : \frac{1!}{b^{1+1}} = \frac{1}{b^2} \quad \text{units} = \text{length}^2$$

$$\text{For } n = 2 : \frac{2!}{b^{2+1}} = \frac{2}{b^3} \quad \text{units} = \text{length}^3$$

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Example: Hydrogen-like ion with charge Z

If you assume that $\psi_{1s} = e^{-\alpha r}$ as a trial function then

$$E_{\text{approx}} = \frac{\int e^{-\alpha r} \hat{H} e^{-\alpha r} dv}{\int e^{-2\alpha r} dv} = T_{\text{approx}} + V_{\text{approx}}$$
$$= \frac{\alpha^2}{2} - \alpha Z$$

in a.u.

where

$$T_{\text{approx}} = \frac{\alpha^2}{2} \quad ; \quad V_{\text{approx}} = -\alpha Z$$

To find α which gives the minimum energy find α for which slope of

$$E(\alpha) = 0$$

$$\frac{dE(\alpha)_{\text{approx}}}{d\alpha} = 0 = \frac{d\left(\frac{\alpha^2}{2} - \alpha Z\right)}{d\alpha} = \alpha - Z$$

So $\alpha = Z$ as you know, is the best form for the hydrogen $1s$, and this

is the exact answer since we lucked out and guessed the exponential

form. If we pick $\psi_{\text{approx}} = e^{-\alpha r}$ we can find a

minimum energy, but it will be higher than $-\frac{1}{2}$ a.u., the exact value.