

Lecture IX

Classical particles

The classical state of a system is specified as giving, at each instant in time, the complete set of coordinates and momenta of the particles, i.e.,

$$\mathbf{r}_1(t), \dots, \mathbf{r}_n(t), \mathbf{p}_1(t), \dots, \mathbf{p}_n(t).$$

If $N=2$, this would be

$$\mathbf{r}_1(t), \mathbf{r}_2(t), \mathbf{p}_1(t), \mathbf{p}_2(t).$$

Suppose the 2-particle system is described as a Hamiltonian of the form

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V(|\mathbf{r}_1 - \mathbf{r}_2|)$$

i.e., the particles are identical (they have the same mass).

Note that if we interchange the labels $1 \leftrightarrow 2$, the Hamiltonian transforms as

$$\tilde{H} = \frac{\mathbf{p}_2^2}{2m} + \frac{\mathbf{p}_1^2}{2m} + V(|\mathbf{r}_2 - \mathbf{r}_1|) = H$$

Thus, H possesses “permutation symmetry.”

Suppose at time t , we say that one particle is at a position \mathbf{r}_a with momentum \mathbf{p}_a and the other is at \mathbf{r}_b with momentum \mathbf{p}_b , we could write down two different mathematical realizations of this physical state:

$$\begin{array}{ll} \mathbf{r}_1(t) = \mathbf{r}_a & \mathbf{r}_2(t) = \mathbf{r}_b \\ \mathbf{p}_1(t) = \mathbf{p}_a & \mathbf{p}_2(t) = \mathbf{p}_b \end{array}$$

or

$$\begin{array}{ll} \mathbf{r}_1(t) = \mathbf{r}_b & \mathbf{r}_2(t) = \mathbf{r}_a \\ \mathbf{p}_1(t) = \mathbf{p}_b & \mathbf{p}_2(t) = \mathbf{p}_a \end{array}$$

which have the same energy because of the permutation symmetry of H .

In addition, any physical property computed from these two representations would be the same, so we can discard one and keep only the other. Thus, we may regard the particles as if they were distinguishable.

Quantum case

In the quantum case, it is clear that we cannot do what we would classically because the particles cannot be described using point positions and momenta, and they do not follow definite trajectories. Rather, they are described as wave functions, and when these wave functions overlap, they mix so that if we make a position measurement and find a value in the overlap region, we cannot say if it is particle 1 that is there or particle 2 if the particles are identical.

Simple example:

Consider 2 spin - $\frac{1}{2}$ particles which are identical. Suppose we observe that one of the particles has an S_z value of $m_a \hbar$ and the other with $m_b \hbar$ such that $m_a \neq m_b$. Is the state vector just after this measurement

$$|\Psi\rangle = \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle \quad \text{or} \quad \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle \quad ?$$

The answer is neither. Unlike in the classical case,

$$\left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle$$

$$\left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle$$

are not physically equivalent since the two states are physically equivalent if they are parallel in the Hilbert space, e.g. two kets

$$|\psi\rangle \quad \text{and} \quad \alpha|\psi\rangle$$

are physically equivalent for any complex number α , but

$$\left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle \neq \alpha \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle$$

That is, permutation cannot be effected by a simple multiplicative operation. However, a state vector

$$\begin{aligned} |\Psi(m_a; m_b)\rangle &\equiv \\ &= C \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle + C' \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle \end{aligned}$$

can be made to satisfy the condition

$$|\Psi(m_a, m_b)\rangle = \alpha |\Psi(m_b, m_a)\rangle$$

This requires:

$$\begin{aligned} &C \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle + C' \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle \\ &= \alpha \left[C \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle + C' \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle \right] \\ &\Rightarrow C = \alpha C' \qquad C' = \alpha C \end{aligned}$$

$$\Rightarrow C' = \alpha^2 C'$$

$$\text{or } \alpha^2 = 1 \Rightarrow \alpha = \pm 1.$$

$$\text{and } C = \pm C'.$$

This gives us two possible physical states:

$$|\Psi_S(m_a, m_b)\rangle \propto \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle + \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle$$

$$|\Psi_A(m_a, m_b)\rangle \propto \left| \frac{1}{2} m_a; \frac{1}{2} m_b \right\rangle - \left| \frac{1}{2} m_b; \frac{1}{2} m_a \right\rangle$$

Suppose, instead, we considered two identical particles moving in one dimension.

If we determined that one particle was at $x=a$ and the other at $x=b$, then there would be two physically equivalent state vectors describing the system just after the measurement, which would be

$$|\Psi_S(a,b)\rangle \propto |a\ b\rangle + |b\ a\rangle$$

or

$$|\Psi_A(a,b)\rangle \propto |a\ b\rangle - |b\ a\rangle$$

New postulate in Quantum Mechanics

A given species of particle will always only be found in either an S-type or an A-type state. In particular, *Fermions* (particles with half integer spin such as electrons, protons, positrons, etc.) are always in antisymmetric states and *Bosons* (particles with integer spin, such as photons, ⁴He atoms, etc.) are always found in symmetric states. Note that if $a=b$,

$$|\Psi_S(a,b)\rangle \propto |a\ a\rangle$$

$$|\Psi_A(a,a)\rangle = 0$$

Thus, for Fermions, two identical Fermions cannot have the same eigenvalue of any operator whose eigenvectors describe the physical state. This is known as the *Pauli exclusion principle*.

Permutation operators

Consider two **distinguishable** quantum particles and an operator Ω whose eigenvectors $|\omega_1\rangle$ we will use to characterize the states of the two particles Hilbert space.

Suppose we perform a measurement and find particle 1 has an eigenvalue ω_1 of the Ω property and particle 2 has a value ω_2 . The state of the system would be (after the measurement)

$$|\Psi(\omega_1, \omega_2)\rangle = |\omega_1\ \omega_2\rangle$$

Define an operator P_{21} whose action on $|\omega_1\ \omega_2\rangle$ is

$$P_{21}|\omega_1\ \omega_2\rangle = |\omega_2\ \omega_1\rangle$$

P_{21} is called the 2-particle *permutation operator*.

Note that if the particles were identical, the physical states would be

$$\begin{aligned} |\Psi_S(\omega_1, \omega_2)\rangle &\propto |\omega_1 \ \omega_2\rangle + |\omega_2 \ \omega_1\rangle \\ |\Psi_A(\omega_1, \omega_2)\rangle &\propto |\omega_1 \ \omega_2\rangle - |\omega_2 \ \omega_1\rangle \end{aligned}$$

Thus,

$$\begin{aligned} P_{21}|\Psi_S(\omega_1, \omega_2)\rangle &\propto P_{21}|\omega_1 \ \omega_2\rangle + P_{21}|\omega_2 \ \omega_1\rangle \\ &= |\omega_2 \ \omega_1\rangle + |\omega_1 \ \omega_2\rangle \\ &= |\Psi_S(\omega_1, \omega_2)\rangle \end{aligned}$$

$$\begin{aligned} P_{21}|\Psi_A(\omega_1, \omega_2)\rangle &\propto P_{21}|\omega_1 \ \omega_2\rangle - P_{21}|\omega_2 \ \omega_1\rangle \\ &= |\omega_2 \ \omega_1\rangle - |\omega_1 \ \omega_2\rangle \\ &= -|\Psi_A(\omega_1, \omega_2)\rangle \end{aligned}$$

Thus, fermionic states are eigenstates of P_{21} with eigenvalue -1, bosonic states have eigenvalue +1. These are the allowed eigenvalues of P_{21} .

Other properties of P_{21} :

1. $(P_{21})^2 = 1$
2. $P_{21}^\dagger = P_{21}$ Hermitian
3. $P_{21}^\dagger P_{21} = I$ Unitary

Symmetizer and antisymmetizer

Consider the operator

$$\begin{aligned} S &= \frac{1}{2}(I + P_{21}) \\ A &= \frac{1}{2}(I - P_{21}) \end{aligned}$$

Given an arbitrary ket $|\psi\rangle$

$S|\psi\rangle$ is symmetric which means

$$P_{21}S|\psi\rangle = S|\psi\rangle \quad (S|\psi\rangle \text{ is an eigenvector of } P_{12} \text{ with eigenvalue} = 1)$$

Proof:
$$\begin{aligned} P_{21}S|\psi\rangle &= P_{21} \frac{1}{2}(I + P_{21})|\psi\rangle = \frac{1}{2}(P_{21} + (P_{21})^2)|\psi\rangle \\ &= \frac{1}{2}(P_{21} + I)|\psi\rangle = S|\psi\rangle \end{aligned}$$

Similarly
$$P_{21}A|\psi\rangle = -A|\psi\rangle$$

Note, given a distinguishable partial state $|\omega_1\omega_2\rangle$ the action of S and A give

$$\begin{aligned} S|\omega_1\omega_2\rangle &= \frac{1}{2}(I + P_{21})|\omega_1\omega_2\rangle = \frac{1}{2}[|\omega_1\omega_2\rangle + |\omega_1\omega_2\rangle] = |\Psi_S(\omega_1\omega_2)\rangle \\ A|\omega_1\omega_2\rangle &= \frac{1}{2}(I - P_{21})|\omega_1\omega_2\rangle = \frac{1}{2}[|\omega_1\omega_2\rangle - |\omega_1\omega_2\rangle] = |\Psi_A(\omega_1\omega_2)\rangle \end{aligned}$$

Properties of A and S:

1. $S^2 = S; A^2 = A$ Idempotent
2. $S^\dagger = S; A^\dagger = A$ Hermitian
3. $S + A = I$
4. $SA = AS = 0$

N-particle states

For an N -particle system, there will be $N!$ total permutations of the particles where, if they are identical, give rise to $N!$ non-equivalent states.

Thus, we need to construct state $|\psi_S\rangle$ for Bosons and $|\psi_A\rangle$ for Fermions which are simultaneous eigenstates of all particle permutation operators P_α , $\alpha = 1, \dots, N!$

$$\begin{aligned} P_\alpha|\psi_S\rangle &= |\psi_S\rangle \\ P_\alpha|\psi_A\rangle &= \varepsilon_\alpha|\psi_A\rangle \end{aligned}$$

where

$$\varepsilon_\alpha = \begin{cases} 1 & \text{where } P_\alpha \text{ is an even permutation} \\ -1 & \text{where } P_\alpha \text{ is an odd permutation.} \end{cases}$$

This can be done by constructing general symmetrizers and anti-symmetrizer operators S and A by

$$S = \frac{1}{N!} \sum_{\alpha=1}^{N!} P_\alpha$$

$$A = \frac{1}{N!} \sum_{\alpha=1}^{N!} \varepsilon_\alpha P_\alpha$$

One term in each sum will be the identity.

For $N=2$, the two permutations are ($\alpha=1 \ 2$ or $\alpha=2 \ 1$)

$$S = \frac{1}{2}(P_{12} + P_{21}) = \frac{1}{2}(I + P_{21})$$

$$A = \frac{1}{2}(\varepsilon_{12}P_{12} + \varepsilon_{21}P_{21})$$

$$P_{12} = I, \varepsilon_{12} = 1$$

$\varepsilon_{21} = -1$ because it is one exchange = odd.

$$A = \frac{1}{2}(I - P_{21})$$

Properties of A, S :

1. $S=S^\dagger \quad A=A^\dagger$
2. $S^2=S \quad A^2=A$
3. $\{S, A\} = 0$.

Although S and A are projectors, for $N>2$, they do **not** project onto complementary spaces.

For $N=2$,

$$S = \frac{1}{2}(I + P_{21})$$

$$A = \frac{1}{2}(I - P_{21})$$

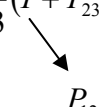
$$S + J = I$$

For $N=3$, there are 6 permutations

$$P_{123}, P_{231}, P_{312}, P_{213}, P_{132}, P_{321}$$

S is a sum of these divided by 6.

$$S + A = \frac{1}{3}(I + P_{231} + P_{312}) \neq I$$



 P_{123}

Thus, the Hilbert space is not composed of the union of a subspace that contains only symmetric states and only anti-symmetric states. There will be overlap and physical states that belong to the overlap region.

Now suppose an operator Ω is used to characterize the state. An N -particle ket

$$|\Psi(\omega_1, \dots, \omega_N)\rangle$$

cannot be used to characterize the states. For correctness, let us consider coordinate space wave functions that also have spin variable. Thus, a wave function

$$\Psi(\mathbf{r}_1, \mathbf{s}_1, \mathbf{r}_2, \mathbf{s}_2, \dots, \mathbf{r}_N, \mathbf{s}_N) \equiv \Psi(1, 2, 3, \dots, N)$$

cannot be used to characterize the states.

However, acting with S or A on the wave function does produce a physical state compounding to the Fermion and Boson species:

$$\Psi_A(1, 2, 3, \dots, N) = A\Psi(1, 2, 3, \dots, N)$$

$$\Psi_S(1, 2, 3, \dots, N) = S\Psi(1, 2, 3, \dots, N)$$

Example: $N=3$.

$$\Psi_A(1,2,3) = \frac{1}{6} [\Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,1,2) - \Psi(3,2,1) - \Psi(1,2,3) - \Psi(2,1,3)]$$

$\Psi_S(1,2,3)$ is the same with all + signs. Note, however, that the state is not properly normalized. To normalize it, the $1/6$ should be replaced by $1/\sqrt{6}$.

Separable Systems

Suppose we have an N -particle Hamiltonian that is completely separable:

$$H = h_1 + h_2 + \dots + h_N \equiv H(1,2,3,\dots,N)$$

where h_i is a single particle Hamiltonian, composed only of 1-body operators and is of the same functional form for each particle.

$$H(1,2,3,\dots,N)\Psi(1,2,3,\dots,N) = E\Psi(1,2,3,\dots,N)$$

would be

$$\Psi(1,2,3,\dots,N) = \psi_1(1)\psi_2(2)\dots\psi_N(N)$$

if the particles were distinguishable.

Then,

$$(h(1) + h(2) + \dots + h(N))\psi_1(1)\psi_2(2)\dots\psi_N(N) = E\psi_1(1)\psi_2(2)\dots\psi_N(N)$$

reduces to a set of single-particle Schrödinger equations

$$h(1)\psi_{\alpha_1}(1) = \varepsilon_{\alpha_1}\psi_{\alpha_1}(1)$$

α_1 is a set of quantum numbers for the one-particle eigenfunction.

$$h(k)\psi_{\alpha_k}(k) = \varepsilon_{\alpha_k}\psi_{\alpha_k}(k)$$

The total energy E is then characterized as

$$E_{\alpha_1\alpha_2\dots\alpha_N} = E_{\alpha_1} + E_{\alpha_2} + \dots + E_{\alpha_N}.$$

$$\psi_{\alpha_1\alpha_2\dots\alpha_N}(1,2,3\dots N) = \psi_{\alpha_1}(1)\psi_{\alpha_2}(2)\dots\psi_{\alpha_N}(N).$$

For identical particles, we cannot use the straight product form of the solutions.

Suppose $N=2$.

For Bosons, we would have

$$\Psi_{s,\alpha_1,\alpha_2}(1,2) = \frac{1}{\sqrt{2}}(\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) + \psi_{\alpha_2}(1)\psi_{\alpha_1}(2))$$

For Fermions,

$$\Psi_{A,\alpha_1,\alpha_2}(1,2) = \frac{1}{\sqrt{2}}(\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) - \psi_{\alpha_2}(1)\psi_{\alpha_1}(2))$$

We showed that $|\psi\rangle$ is an eigenfunction of P_{21} , hence $|\psi\rangle + P_{21}|\psi\rangle$ is also an eigenfunction of P_{21} .

Let's show it explicitly:

$$\begin{aligned} H\Psi_{A,\alpha_1,\alpha_2}(1,2) &= \frac{1}{\sqrt{2}}(h(1) + h(2))(\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) - \psi_{\alpha_2}(1)\psi_{\alpha_1}(2)) \\ &= \frac{1}{\sqrt{2}}[(h(1))\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) + \psi_{\alpha_1}(1)h(2)\psi_{\alpha_2}(2) - h(1)\psi_{\alpha_2}(1)\psi_{\alpha_1}(2) - \psi_{\alpha_2}(1)(h(2)\psi_{\alpha_1}(2))] \\ &= \frac{1}{\sqrt{2}}[\varepsilon_{\alpha_1}\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) + \varepsilon_{\alpha_2}\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) - \varepsilon_{\alpha_2}\psi_{\alpha_2}(1)\psi_{\alpha_1}(2) - \varepsilon_{\alpha_1}\psi_{\alpha_2}(1)\psi_{\alpha_1}(2)] \\ &= \frac{1}{\sqrt{2}}[(\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2})(\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) - \psi_{\alpha_2}(1)\psi_{\alpha_1}(2))] \\ &\Rightarrow E_{\alpha_1\alpha_2} = \varepsilon_{\alpha_1} + \varepsilon_{\alpha_2} \end{aligned}$$

Note that in the antisymmetric case:

$$\begin{aligned}\Psi_{A,\alpha_1,\alpha_2}(1,2) &= \frac{1}{\sqrt{2}}(\psi_{\alpha_1}(1)\psi_{\alpha_2}(2) - \psi_{\alpha_2}(1)\psi_{\alpha_1}(2)) \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{\alpha_1}(1) & \psi_{\alpha_1}(2) \\ \psi_{\alpha_2}(1) & \psi_{\alpha_2}(2) \end{vmatrix}\end{aligned}$$

called a *Slater determinant*.

For an N -particle antisymmetric state:

$$\begin{aligned}\Psi_{A,\alpha_1,\alpha_2,\dots,\alpha_N}(1,\dots,N) \\ = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(1) & \dots & \psi_{\alpha_1}(N) \\ \vdots & \ddots & \vdots \\ \psi_{\alpha_N}(1) & \dots & \psi_{\alpha_N}(N) \end{vmatrix}\end{aligned}$$

Clearly, we cannot have more than one particle in the same state (with the same set of quantum numbers) or else two rows of the matrix will be the same and the determinant will vanish. Hence, it satisfies the Pauli exclusion principle.

Occupation numbers and second quantization

Total energy is given by

$$E_{\alpha_1 \dots \alpha_N} = \sum_i \varepsilon_{\alpha_i}$$

An alternative way of thinking about N -particle states is to view $\psi_{\alpha}(\mathbf{x})$ as a state that can be **occupied** with energy ε_{α} .

Let f_{α} be the number of particles occupying the state. Then,

$$\begin{aligned}\sum_{\alpha} f_{\alpha} &= N \\ E_{\{f_{\alpha}\}} &= \sum_{\alpha} f_{\alpha} \varepsilon_{\alpha}\end{aligned}$$

Many-particle states:

$$|f_1 f_2 f_3 \dots\rangle$$

Creation and annihilation operators

Bosons: $f_\alpha = 0, 1, 2, \dots$

$$b_\alpha |f_1 f_2 f_3 \dots f_\alpha \dots\rangle = \sqrt{f_\alpha} |f_1 f_2 f_3 \dots f_\alpha - 1 \dots\rangle$$

$$b_\alpha^\dagger |f_1 f_2 f_3 \dots f_\alpha \dots\rangle = \sqrt{f_\alpha + 1} |f_1 f_2 f_3 \dots f_\alpha + 1 \dots\rangle$$

$$b_\alpha^\dagger b_\alpha |f_1 f_2 f_3 \dots f_\alpha \dots\rangle = f_\alpha |f_1 f_2 f_3 \dots f_\alpha \dots\rangle$$

$$[b_\alpha, b_{\alpha'}^\dagger] = \delta_{\alpha\alpha'}$$

Fermions: $f_\alpha = 0, 1$

$$a_\alpha |f_1 f_2 f_3 \dots f_\alpha = 1 \dots\rangle = (-1)^{N_\alpha} |f_1 f_2 f_3 \dots f_\alpha = 0 \dots\rangle$$

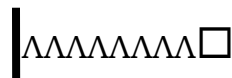
$$a_\alpha^\dagger |f_1 f_2 f_3 \dots f_\alpha = 0 \dots\rangle = (-1)^{N_\alpha} |f_1 f_2 f_3 \dots f_\alpha = 1 \dots\rangle$$

$$N_\alpha = \sum_{\beta=1}^{\alpha=1} f_\beta$$

$$[a_\alpha, a_{\alpha'}^\dagger]_{\pm} = \delta_{\alpha\alpha'}$$

When can we ignore symmetrization/antisymmetrization?

In classical mechanics, if we are interested in the motion of a mass on a spring



in calculating its motion, we usually ignore such efforts as the pull of gravity of the other planets in the solar system.

This is an approximation, albeit a good one!

Neglecting effects such as this is tantamount to assuming that the Hamiltonian is separable into system and rest of universe components

$$H_{uni} = H_{sys} + H_{rest}$$

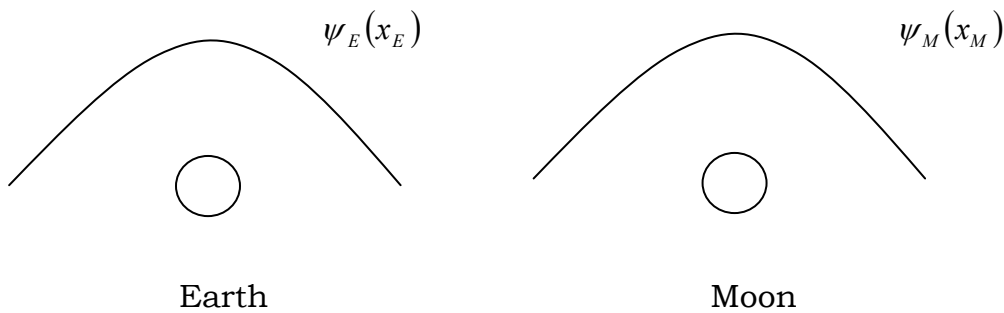
In Quantum Mechanics, this means that the wave function is separable into (*sys*) and (*rest*) components

$$\Psi(x_{sys}, x_{rest}) = \psi_{sys}(x_{sys}) \psi_{rest}(x_{rest})$$

$$\begin{aligned}\Rightarrow P(x_{sys}) &= |\psi_{sys}(x_{sys})|^2 \left[\int dx_{rest} |\psi(x_{rest})|^2 \right] \\ &= |\psi_{sys}(x_{sys})|^2\end{aligned}$$

When we have identical particles, however, simple product forms no longer work.

Consider an example of two Bosons, one on Earth, one on the moon.



$$\Psi(x_E, x_M) \propto \psi_E(x_E)\psi_M(x_M) \pm \psi_E(x_M)\psi_M(x_E)$$

However, if the two particles are very far apart, we expect:

$$\begin{aligned}\psi_E(x_M) &\approx 0 \\ \psi_M(x_E) &\approx 0\end{aligned}$$

$$\Psi(x_E, x_M) \propto \psi_E(x_E)\psi_M(x_M)$$

Role of temperature

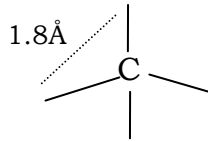
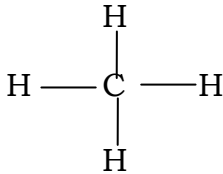
Temperature causes quantum localization to decrease as temperature is increased.

The thermal wavelength

$$\lambda = \sqrt{\frac{\hbar^2}{2\pi mkT}}$$

k is Boltzmann's constant.

Consider methane: CH_4



The four Hs are identical. Do we need to consider the symmetry of the wave function at 300k? The thermal wavelength is:

$$\lambda = \sqrt{\frac{1}{2 \cdot \pi \cdot 1836 \text{amu} \cdot 9.5 \times 10^{-4} \text{Ha}}}$$

$$\lambda = 0.3 \text{ bohr} = 0.16 \text{ \AA}$$

No!

What about 4k?

$$\lambda = \sqrt{\frac{1}{2 \cdot \pi \cdot 1836 \text{amu} \cdot 1.3 \times 10^{-5} \text{Ha}}}$$

$$= 2.6 \text{ bohr} = 1.4 \text{ \AA}$$

Yes!

For an electron at 300k

$$\lambda = \sqrt{\frac{1}{2\pi \cdot 9.5 \times 10^{-4}}} = 12.9 \text{ bohr} = 7 \text{ \AA}$$

Electrons are delocalized over large portions of molecules!