EE201/MSE207 Lecture 12

Two-particle systems (Ch. 5)

Generalization to two-particles is very natural.

A two-particle state is characterized by wavefunction $\Psi(\vec{r}_1, \vec{r}_2, t)$
(for a moment forget about spin)

SE: $$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \qquad \hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

$$\frac{\partial^2}{\partial x_1} + \frac{\partial^2}{\partial y_1} + \frac{\partial^2}{\partial z_1}$$ (Laplacian)

$|\Psi|^2$: probability density

Normalization $$\int |\Psi|^2 \, d\vec{r}_1 d\vec{r}_2 = 1$$

If $V(\vec{r}_1, \vec{r}_2)$ (no time dependence for potential energy), then TISE: $\hat{H}\psi = E\psi$

Then general solution of SE:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \sum_n c_n \psi_n(\vec{r}_1, \vec{r}_2)\, e^{-i\frac{E_n}{\hbar}t} \qquad \sum_n |c_n|^2 = 1$$

Simplification if $V = V(\vec{r}_1 - \vec{r}_2)$

Then the problem reduces to one-particle problem (may be important for excitons)

Similar situation in astronomy: two-body problem is essentially one-body problem

Classical mechanics

Introduce two variables (new coordinates):

center of mass $\vec{R} = \dfrac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$ (moves freely by inertia)

difference $\vec{r} = \vec{r}_1 - \vec{r}_2$

Evolution of $\vec{r}$: Force $\vec{F} = -\nabla V(\vec{r})$ acts on both particles

$$\ddot{\vec{r}} = \frac{\vec{F}}{m_1} + \frac{\vec{F}}{m_2} = \vec{F}\,\frac{m_1 + m_2}{m_1 m_2} = \frac{\vec{F}}{\mu} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Therefore, evolution of $\vec{r}$ is as for a mass μ in potential V
(this is how Earth-Moon problem is analyzed)

Quantum mechanics for $V = V(\vec{r}_1 - \vec{r}_2)$

$$\hat{H} = -\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(\vec{r})$$

Kinetic energy for mass $m_1 + m_2$ at center of mass, kinetic energy of mass μ at position difference, and potential energy

Derivation

$$\frac{\partial}{\partial r_1} = \frac{\partial}{\partial R}\frac{\partial R}{\partial r_1} + \frac{\partial}{\partial r}\frac{\partial r}{\partial r_1} = \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial R} + \frac{\partial}{\partial r}$$

$$\frac{\partial}{\partial r_2} = \frac{m_2}{m_1 + m_2}\frac{\partial}{\partial R} - \frac{\partial}{\partial r}$$

$$\frac{\partial^2}{\partial r_1^2} = \left(\frac{m_1}{m_1 + m_2}\right)^2 \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} + \frac{2m_1}{m_1 + m_2}\frac{\partial^2}{\partial r\,\partial R}$$

$$\frac{\partial^2}{\partial r_2^2} = \left(\frac{m_2}{m_1 + m_2}\right)^2 \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} - \frac{2m_2}{m_1 + m_2}\frac{\partial^2}{\partial r\,\partial R}$$

Separation of variables

$$\psi = \psi_R(\vec{R})\,\psi_r(\vec{r}) \qquad E = E_R + E_r$$

E_R is kinetic energy of free particle with mass $m_1 + m_2$

For E_r we need to solve TISE $$-\frac{\hbar^2}{2\mu}\nabla^2\psi_r(\vec{r}) + V(\vec{r})\,\psi_r(\vec{r}) = E_r\,\psi_r(\vec{r})$$

If $V \neq V(\vec{r})$, then need to solve much more complicated 2-particle TISE

Identical particles

In quantum mechanics two electrons are indistinguishable (postulate), similarly two protons, two holes, etc.
Surprisingly, this leads to non-trivial consequences.

Simple case (two particles in two states, no interaction, no spin)

$$\psi(\vec{r}_1,\vec{r}_2)=\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2)$$

First particle in state a, second one in state b (distinguishable particles)

However, for indistinguishable particles $\psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)$ corresponds to the same state

Actually, such state is described by wavefunction

$$\psi_\pm(\vec{r}_1,\vec{r}_2)=\frac{1}{\sqrt{2}}\left[\,\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2)\pm\psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)\,\right]$$

$+$ for bosons (integer spin),
$-$ for fermions (half-integer spin)

Generally

$$\psi(\vec{r}_1,\vec{r}_2)=\pm\psi(\vec{r}_2,\vec{r}_1)$$

($+$ for bosons, $-$ for fermions)

Symmetry for identical particles

Generally (no spin, i.e. the same spin)

$\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)$ (+ for bosons, − for fermions)

(new development: “anyons”)

With spin

$\psi(\vec{r}_1, S_1, \vec{r}_2, S_2) = \pm\psi(\vec{r}_2, S_2, \vec{r}_1, S_1)$

(exchange of two particles)

Proof

Introduce exchange operator $\hat{P}$. It satisfies $\hat{P}^2 = \hat{1}$ and commutes with $\hat{H}$.
Therefore common eigenstates, $\lambda^2 = 1 \Rightarrow \lambda = \pm 1$.

Remark: no such symmetry for different particles (e.g., proton and electron)

Pauli exclusion principle

Two fermions cannot occupy the same state (“cannot sit on the same chair”)

Proof: otherwise $\psi = 0$

This symmetry changes average distance between particles
(exchange correlation, “exchange interaction”)

Simple example of exchange correlation

Consider two particles in 1D, occupying states a and b.

3 cases

(1) $\psi = \psi_a(x_1)\,\psi_b(x_2)$ — distinguishable particles

(2) $\psi = \frac{1}{\sqrt{2}}[\psi_a(x_1)\,\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]$ — bosons

(3) $\psi = \frac{1}{\sqrt{2}}[\psi_a(x_1)\,\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]$ — fermions

Let us show that bosons are closer to each other, fermions are farther away.

Calculate $\langle (x_1 - x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle$

Case (1): distinguishable

$$\langle x_1^2\rangle = \iint x_1^2\,|\psi(x_1,x_2)|^2\,dx_1 dx_2 = \int x_1^2\,|\,\psi_a(x_1)|^2 dx_1\ \int|\psi_b(x_2)|^2 dx_2 =$$

$$= \langle x^2\rangle_a \times 1 = \langle x^2\rangle_a$$

Similarly $\langle x_2^2\rangle = \langle x^2\rangle_b$

$$\langle x_1 x_2\rangle = \iint x_1 x_2\,|\psi(x_1,x_2)|^2\,dx_1 dx_2 =$$

$$= \int x_1|\,\psi_a(x_1)|^2 dx_1\ \int x_2|\psi_b(x_2)|^2 dx_2 = \langle x\rangle_a\langle x\rangle_b$$ (uncorrelated)

Simple example of exchange correlation (cont.)

Case (2): bosons $\psi = \frac{1}{\sqrt{2}}[\psi_a(x_1)\,\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]$

$$\langle x_1^2 \rangle = \iint x_1^2\, |\psi(x_1, x_2)|^2\, dx_1 dx_2 =$$

$$= \frac{1}{2}\int x_1^2\, |\psi_a(x_1)|^2 dx_1 \underbrace{\int |\psi_b(x_2)|^2 dx_2}_{1} + \frac{1}{2}\int x_1^2\, |\psi_b(x_1)|^2 dx_1 \underbrace{\int |\psi_a(x_2)|^2 dx_2}_{1}$$

$$+ \frac{1}{2}\int x_1^2\ \psi_a^*(x_1)\,\psi_b(x_1)\,dx_1 \underbrace{\int \psi_b^*(x_2)\psi_a(x_2)\,dx_2}_{0} +$$

$$+ \frac{1}{2}\int x_1^2\ \psi_b^*(x_1)\,\psi_a(x_1)\,dx_1 \underbrace{\int \psi_a^*(x_2)\psi_b(x_2)\,dx_2}_{0} =$$

$$= \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b)$$

Similarly $\langle x_2^2 \rangle = \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b)$

(quite natural, since each particle in both states)

Simple example of exchange correlation (cont.)

Case (2): bosons $\psi = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\,\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right]$

$$\langle x_1^2\rangle = \langle x_2^2\rangle = \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right)$$

$$\langle x_1 x_2\rangle = \iint x_1 x_2\,|\psi(x_1, x_2)|^2\,dx_1 dx_2 =$$

$$= \frac{1}{2}\underbrace{\int x_1\,|\psi_a(x_1)|^2 dx_1}_{\langle x\rangle_a}\,\underbrace{\int x_2\,|\psi_b(x_2)|^2 dx_2}_{\langle x\rangle_b} +$$

$$+\frac{1}{2}\int x_1|\psi_b(x_1)|^2 dx_1\,\int x_2\,|\psi_a(x_2)|^2 dx_2 + \quad \Big\}\ \text{same as line 1}$$

$$+\frac{1}{2}\underbrace{\int x_1\,\psi_a^*(x_1)\,\psi_b(x_1)\,dx_1}_{}\,\underbrace{\int x_2\,\psi_b^*(x_2)\,\psi_a(x_2)\,dx_2}_{} +$$

conjugate

$$\text{same as line 3}\ \Big\{ +\frac{1}{2}\int x_1\,\psi_b^*(x_1)\,\psi_a(x_1)\,dx_1\int x_2\,\psi_a^*(x_2)\,\psi_b(x_2)\,dx_2 =$$

$$= \langle x\rangle_a\langle x\rangle_b + \underbrace{\left|\int x\,\psi_a^*(x)\,\psi_b(x)\,dx\right|^2}_{\text{exchange term}}$$

Simple example of exchange correlation: summary

Case (1): distinguishable particles $\psi = \psi_a(x_1)\,\psi_b(x_2)$

$$\langle x_1^2\rangle = \langle x^2\rangle_a \qquad \langle x_2^2\rangle = \langle x^2\rangle_b \qquad \langle x_1 x_2\rangle = \langle x\rangle_a \langle x\rangle_b$$

Case (2): bosons $\psi = [\psi_a(x_1)\,\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]/\sqrt{2}$

$$\langle x_1^2\rangle = \langle x_2^2\rangle = \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right)$$

$$\langle x_1 x_2\rangle = \langle x\rangle_a \langle x\rangle_b + \left|\int x\,\psi_a^*(x)\,\psi_b(x)\,dx\right|^2$$

Case (3): fermions $\psi = [\psi_a(x_1)\,\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]/\sqrt{2}$

$$\langle x_1^2\rangle = \langle x_2^2\rangle = \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right)$$

$$\langle x_1 x_2\rangle = \langle x\rangle_a \langle x\rangle_b - \left|\int x\,\psi_a^*(x)\,\psi_b(x)\,dx\right|^2$$

If $\psi_a(x)$ and $\psi_b(x)$ do not overlap, then no difference.

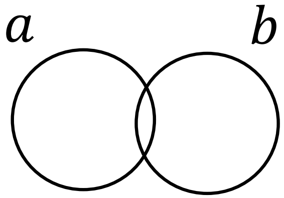
If $\psi_a(x)$ and $\psi_b(x)$ overlap, then exchange term is non-zero.

For case 2 (bosons), $\langle x_1 x_2\rangle$ is larger $\Rightarrow$ $\langle (x_1 - x_2)^2\rangle$ is smaller (closer to each other)

For case 3 (fermions), $\langle (x_1 - x_2)^2\rangle$ is larger (like to be farther away from each other)

Exchange correlation (“exchange interaction”, “exchange force”)

Molecule of hydrogen (H_2)



Now need to take spin into account

What is spin state of the ground state? (Show that singlet)

Ground state: both electrons have $n = 1$, but also have spins

If total spin is 0 (singlet), then spin state is $\frac{\uparrow\downarrow-\downarrow\uparrow}{\sqrt{2}}$ (antisymmetric to exchange), therefore spatial part should be symmetric (so that total is antisymmetric),

therefore case (2) $\Rightarrow$ electrons closer to each other $\Rightarrow$ covalent bond

(actually, electrons repel each other, but attraction to protons is more important)

If total spin is 1 (triplet), then spin state is $\uparrow\uparrow$ or $\downarrow\downarrow$ or $\frac{\uparrow\downarrow+\downarrow\uparrow}{\sqrt{2}}$ (all symmetric), therefore spatial part is antisymmetric (case 3)

$\Rightarrow$ electrons are farther away from each other $\Rightarrow$ antibonding state (not stable)

Ground state wavefunction

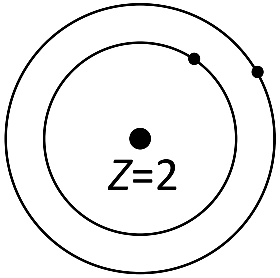
$$\psi = \frac{1}{\sqrt{2}}\left[\,\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)\,\right]\frac{\uparrow\downarrow-\downarrow\uparrow}{\sqrt{2}}$$

Atoms (many electrons)

$$\hat{H} = \sum_{j=1}^{Z}\left(-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{\left|\vec{r_j}\right|}\right) + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{j\neq k}^{Z}\frac{e^2}{\left|\vec{r_j} - \vec{r_k}\right|}$$

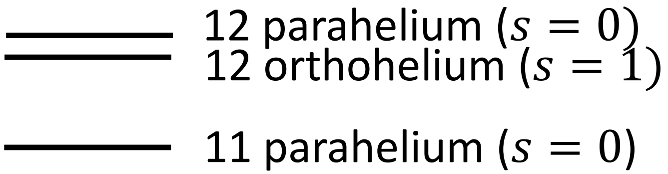
and wavefunction must be antisymmetric for exchange of any two electrons (exchange of both positions and spins)

Atom of helium (He)



What are spins of lowest energy states?

If we neglect *e*-*e* interaction (approximation), then just two electrons in hydrogen-like atom ($Z = 2$ instead of $Z = 1$)



12 parahelium ($s = 0$)
12 orthohelium ($s = 1$)

11 parahelium ($s = 0$)

Ground state ($n = 1$ and $n = 1$) $\Rightarrow$ symmetric spatial part of wavefunction $\Rightarrow$ antisymmetric spin part, i.e. $s = 0$ (singlet, parahelium) $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$

First excited state ($n = 1$ and $n = 2$)

If $s = 0$ (singlet, parahelium) $\Rightarrow$ spin part of wavefunction is antisymmetric
$\Rightarrow$ spatial part is symmetric $\Rightarrow$ electrons closer to each other
$\Rightarrow$ higher energy of *e*-*e* interaction $\Rightarrow$ higher energy

If $s = 1$ (triplet, orthohelium) $\Rightarrow$ spin part is symmetric $\Rightarrow$ spatial part is antisymmetric $\Rightarrow$ electrons farther away $\Rightarrow$ lower energy