Eigenstates for the dipole-dipole interaction.

5) We return to the dipole-dipole interaction outlined on p. ip2, Eqs. (3) & (4). Suppose the particles are electrons, i.e. identical fermions each with spin $\frac{1}{2}$. The overall system eigenfcns must accommodate the following eigenvalues:

$$\rightarrow S_1 = S_2 = \frac{1}{2} \Rightarrow \left\{ \begin{array}{ll} \text{total spin}: & S = S_1 + S_2, \ldots, |S_1 - S_2| = 1 \;\&\; 0; \\ \text{spin projection}: & m = m_1 + m_2 = \left\{ \begin{array}{l} 1, 0, -1, \text{ for } S = 1; \\ 0, \text{ only, for } S = 0. \end{array} \right. \end{array} \right. \quad (15)$$

So there are 4 eigenstates $|S, m\rangle$, which can be constructed from products of the individual spin eigenfcns: $\alpha(k) = |S_k = \frac{1}{2}, m_k = +\frac{1}{2}\rangle$ (spin up) & $\beta(k) = |S_k = \frac{1}{2}, m_k = -\frac{1}{2}\rangle$ (spin down), for the k^{th} particle, $k = 1 \;\&\; 2$. We find by standard procedures [Davydov, Sec. 72; Sakurai, Sec. 3.7]:

$$\left. \begin{array}{l} \left. \begin{array}{l} |S=1, m=+1\rangle = \alpha(1)\alpha(2), \\ |S=1, m=0\rangle = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)], \\ |S=1, m=-1\rangle = \beta(1)\beta(2); \end{array} \right\} \text{spin TRIPLET} \\ \text{and } \left. |S=0, m=0\rangle = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \right\} \text{spin SINGLET} \end{array} \right\} \quad (16)$$

These eigenstates are constructed (via a Clebsch-Gordan transform) so as to be mutually orthogonal. But notice that they have a built-in exchange symmetry:

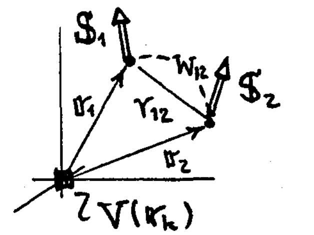
$$\text{under exchange of particles } 1 \;\&\; 2 \left\{ \begin{array}{ll} |S=1, m\rangle \rightarrow (+)|S=1, m\rangle \ldots\ldots & \text{TRIPLET state has \underline{even} exchange symmetry;} \\ |S=0, m=0\rangle \rightarrow (-)|S=0, m=0\rangle \ldots & \text{SINGLET state has \underline{odd} exchange symmetry.} \end{array} \right. \quad (17)$$

That the $|S, m\rangle$ states do have an exchange symmetry is required by the fact that the system Ham$^{\underline{n}}$ [Eq. (4)] is exchange invariant: $\mathcal{H}(2,1) = \mathcal{H}(1,2)$.

$\boxed{\text{NOTE}}$ Only $|S=0, m=0\rangle$ has the $(-)$ exchange symmetry needed to describe fermions. Does this mean that two electrons must always be found in a state where $S = S_1 + S_2 = 0$? No... because the total wavefcn includes a space dependence: $\Psi(1,2) = u(\mathbf{r}_1, \mathbf{r}_2)|S, m\rangle$. Then $\Psi(2,1) = (-)\Psi(1,2)$ is achieved by choosing $u(\mathbf{r}_2, \mathbf{r}_1) = \mp u(\mathbf{r}_1, \mathbf{r}_2)$ for $\begin{array}{l}\text{TRIPLETS} \\ \text{SINGLETS}\end{array}$.

Symmetrization of space wavefcns for two weakly interacting particles.

6) A dramatic example of the <u>physical</u> effects of the symmetrization postulate is provided by looking in more detail at a system of two identical particles (fermions <u>or</u> bosons) that interact by both their space and spin coordinates. Have:



interaction between two identical particles

total Ham^n: $\mathcal{H}(\mathbb{p}_1,\mathbb{r}_1,\sigma_1;\mathbb{p}_2,\mathbb{r}_2,\sigma_2) = H_1 + H_2 + W_{12}$,
σ_k represents spin state $|S_k, m_k\rangle$

w/ $H_k = \frac{1}{2m}\mathbb{p}_k^2 + V(\mathbb{r}_k)$ ✓ individual binding of k^{th} particle ($k=1$ & 2) to potential V,

$W_{12} = W(\mathbb{r}_1,\sigma_1;\mathbb{r}_2,\sigma_2)$ ← particle-particle interaction. (18)

Suppose the inter-particle coupling W_{12} is <u>separately</u> invariant under exchange of space cds $(\mathbb{p}_k, \mathbb{r}_k)$ and spin cds σ_k. Then so is $\mathcal{H}$. An example is...

$$\rightarrow W_{12} = \text{dipole-dipole interaction [Eq.(3)]} + \frac{q^2}{r_{12}}, \tag{19}$$

where the term in q is the Coulomb repulsion between the particles, each assumed to have charge q, and $r_{12} = |\mathbb{r}_1 - \mathbb{r}_2|$ is the inter-particle distance. Clearly $W_{21} = W_{12}$ when <u>either</u> the spins $\mathbb{S}_1$ & $\mathbb{S}_2$ are exchanged, <u>or</u> the space cds $\mathbb{r}_1$ & $\mathbb{r}_2$ are exchanged, or both cds together. Now when the system eigenstates are written as products (in the so-called "coupled representation"):

$$\rightarrow \Psi(\mathbb{r}_1,\sigma_1;\mathbb{r}_2,\sigma_2) = u(\mathbb{r}_1,\mathbb{r}_2)\,\chi(\sigma_1,\sigma_2) \quad \checkmark \; u = \text{space eigenstate}, \; \chi = \text{spin eigenstate},^{\bigstar}$$

$$\mathcal{H}\text{ separately invariant for space \& spin exchange} \Longrightarrow \left\{\begin{array}{l} u(\mathbb{r}_2,\mathbb{r}_1) = \pm\, u(\mathbb{r}_1,\mathbb{r}_2) \\ \chi(\sigma_2,\sigma_1) = \pm\,\chi(\sigma_1,\sigma_2)\end{array}\right\| \;\text{\underline{both} } u \text{ \& } \chi \text{ have } \pm \text{ exchange symmetry.} \tag{20}$$

For BOSONS, w/ $\Psi(2,1) = +\Psi(1,2)$, both u & χ must have the <u>same</u> exchange symmetry (both + or both −). For FERMIONS, w/ $\Psi(2,1) = -\Psi(1,2)$ required, u & χ must have <u>opposite</u> exchange symmetries (one +, the other −). So far, there are no surprises, just bookkeeping.

★ For two spin ½ fermions, the $\chi(\sigma_1,\sigma_2)$ are just the eigenstates $|S,m\rangle$ of Eq. (16)

Consequences of symmetrized space states.

The surprise comes when we look at some consequences of the symmetrized space eigenstate $u(\mathbf{r}_1, \mathbf{r}_2)$. If one particle is in state α (e.g. an α "orbital") and the other in state $\beta \neq \alpha$ (a β "orbital"), then the space eigenstate must be:

$$\rightarrow u^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \pm \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2)\right] \quad (21)$$

$\surd$ $u^\pm$ has $\pm$ exchange symmetry for $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$.

The ϕ's are eigenfcns of $\mathcal{H}_0$ in Eq. (18). If W_{12} is "weak", the ϕ's are $\simeq$ eigenfcns of H [i.e. $H_k \phi_\alpha(\mathbf{r}_k) \simeq E_\alpha \phi_\alpha(\mathbf{r}_k)$, etc.].

Now we calculate the expectation value of the interparticle separation in the eigenstates $u^\pm$ of Eq. (21). That is, we calculate...

$$\rightarrow \langle r_{12}^2 \rangle_\pm = \langle u^\pm | r_{12}^2 | u^\pm \rangle = \int d^3x_1 \int d^3x_2\, u^{\pm *}(\mathbf{r}_1, \mathbf{r}_2)\left[(\mathbf{r}_1 - \mathbf{r}_2)^2\right] u^\pm(\mathbf{r}_1, \mathbf{r}_2). \quad (22)$$

both + signs together, or both (−) signs (i.e. $\langle u^+ | r_{12}^2 | u^+ \rangle$, or $\langle u^- | r_{12}^2 | u^- \rangle$).

Plug $u^\pm$ of (21) into (22), expand, and use orthogonality of ϕ_α & ϕ_β to get:

$$\boxed{\langle r_{12}^2 \rangle_\pm = \left[\langle r^2 \rangle_\alpha + \langle r^2 \rangle_\beta - 2\langle \mathbf{r} \rangle_\alpha \cdot \langle \mathbf{r} \rangle_\beta\right] \mp 2\left|\langle \alpha | \mathbf{r} | \beta \rangle\right|^2} \quad (23)$$

$\mathcal{W}$ $\langle r^2 \rangle_\alpha = \int d^3x\, \phi_\alpha^*(\mathbf{r})\{r^2\}\phi_\alpha(\mathbf{r})$, similarly for $\langle r^2 \rangle_\beta$, etc.

and: $\langle \alpha | \mathbf{r} | \beta \rangle = \int d^3x\, \phi_\alpha^*(\mathbf{r})\{\mathbf{r}\}\phi_\beta(\mathbf{r})$ $\surd$ this is called an "exchange integral".

REMARKS on the interparticle distance r_{12}.

1. Of course $u^\pm$ of Eq. (21) must be used if the particles we are dealing with are identical (indistinguishable) and the system Hamⁿ is exchange invariant. But if the particles were distinguishable, we could have used the simple product; $u^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$. Then in (23), we would have gotten:

$$\rightarrow \langle r_{12}^2 \rangle_0 = \left[\langle r^2 \rangle_\alpha + \langle r^2 \rangle_\beta - 2\langle \mathbf{r} \rangle_\alpha \cdot \langle \mathbf{r} \rangle_\beta\right]. \quad (24)$$

This is the QM equivalent of $r_{12}^2 = (\mathbf{r}_\alpha - \mathbf{r}_\beta)^2$, and it constitutes just the first 3 terms RHS in (23). The term in $\langle \alpha | \mathbf{r} | \beta \rangle$ is distinctly a "new toy".

Symmetrized space states and exchange forces. He atom example.

REMARKS on r_{12} (cont'd)

2. Incorporate (24) in (23), so as to write...

particles indistinguishable ⇒ exchange symmetry imposed on eigenstate $u(\mathbf{r}_1, \mathbf{r}_2)$.

$$\langle r_{12}^2 \rangle_\pm = \langle r_{12}^2 \rangle_0 \mp 2\,|\langle \alpha | \mathbf{r} | \beta \rangle|^2. \quad (25)$$

particles distinguishable; no symmetry for $u(\mathbf{r}_1, \mathbf{r}_2)$.

exchange term

This conclusion is inescapable: the requirement of exchange symmetry for the space eigenstate $u(\mathbf{r}_1, \mathbf{r}_2)$ actually alter the interparticle distance r_{12}!

This result is semi-astonishing (and peculiarly QM-cal): particles "forced" by exchange symmetry requirements into an even space state u^+ actually end up closer together on the average than particles which must occupy an odd space state u^-. The exchange symmetry requirement is equivalent to an "exchange force"...

$$\rightarrow \text{EXCHANGE SYMMETRY} \leftrightarrow \text{EXCHANGE FORCE} \begin{cases} \text{attractive for even space states } u_+, \\ \text{repulsive for odd space states } u_-. \end{cases} \quad (26)$$

The effects of this exchange force, in moving the particles around, is present just as surely as though we had added additional terms to the Hamiltonian $\mathcal{H}$. And the exchange forces have a great deal to do with explaining the observed structure of multi-electron atoms, covalent bonding in molecules, etc. These QM structures are -- in some deep sense -- just the inevitable consequences of requiring exchange symmetry as a "constant-of-the-motion" for systems of identical (indistinguishable) particles.

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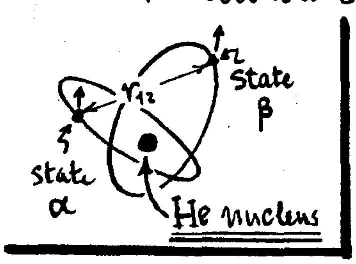
7) As a more specific example of exchange effects, we return to the He atom -- mentioned briefly in Eq. (9) above. Write the total Hamⁿ $\mathcal{H}$ as...



$$\mathcal{H}(1,2) = H(1) + H(2) + \frac{e^2}{r_{12}}. \quad (27)$$

Coulomb Hamⁿs: $H(k) = \frac{1}{2m}\mathbf{p}_k^2 + V(\mathbf{r}_k)$.

e-e repulsion

$\mathcal{H}(1,2)$ ignores the electron magnetic dipole-dipole interaction, which is "small" (in energy terms).