1. Exchange operator is defined as

$$(P_{12}f)(x_1, x_2) = f(x_2, x_1)$$

Prove that the exchange operator P_{12} is hermitian

solution

$$\begin{aligned}\langle f|P_{12}|g\rangle &= \int dx_1 \int dx_2 f^*(x_1, x_2) g(x_2, x_1) \\ &= \int dx_2 \int dx_1 f^*(x_2, x_1) g(x_1, x_2) \\ &= \left(\int dx_2 \int dx_1 g^*(x_1, x_2) f(x_2, x_1)\right)^* \\ &= \langle g|P_{12}|f\rangle^*\end{aligned}$$

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2. Show that following two-spin states are eigenstates of $\mathbf{S^2}$, $\mathbf{S_z}$ and P_{12} operators, where $\mathbf{S} = \mathbf{S_1} + \mathbf{S_2}$:

(a) $\alpha(1)\alpha(2)$ (b) $\beta(1)\beta(2)$

(c) $(\alpha(1)\beta(2) - \beta(1)\alpha(2))/\sqrt{2}$ (d) $(\alpha(1)\beta(2) + \beta(1)\alpha(2))/\sqrt{2}$

solution

Note that $\mathbf{S}^2 = 3\hbar^2/2 + (\mathbf{S}_1^+\mathbf{S}_2^- + \mathbf{S}_1^-\mathbf{S}_2^+) + 2\mathbf{S}_1^z\mathbf{S}_2^z$.

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3. Consider two spin-1 particles. Let $\alpha = |1,1\rangle$, $\beta = |1,0\rangle$ and $\delta = |1,-1\rangle$. Find the eigenstates of $\mathbf{S^2}$, $\mathbf{S_z}$ and P_{12} operators, where $\mathbf{S} = \mathbf{S_1} + \mathbf{S_2}$:

solution

$$\begin{aligned}|2,2\rangle &= \alpha(1)\alpha(2) \\ |2,1\rangle &= (\alpha(1)\beta(2) + \beta(1)\alpha(2))/\sqrt{2} \\ |2,0\rangle &= (\alpha(1)\delta(2) + \delta(1)\alpha(2) + 2\beta(1)\beta(2))/\sqrt{6} \\ |1,1\rangle &= (\alpha(1)\beta(2) - \beta(1)\alpha(2))\sqrt{2} \\ |1,0\rangle &= (\alpha(1)\delta(2) - \delta(1)\alpha(2))/\sqrt{2} \\ |0,0\rangle &= (\alpha(1)\delta(2) + \delta(1)\alpha(2) - \beta(1)\beta(2))/\sqrt{3}\end{aligned}$$

The state $|2,1\rangle$ can be obtained from $\mathbf{S}^- |\mathbf{2},\mathbf{2}\rangle$. The state $|2,1\rangle$ can be obtained by orthogonalizing it with $|2,1\rangle$.

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4. Two non-interacting identical particles are enclosed in a 1D box of length L. What is the energy of the ground state and the first excited state? Find the degeneracies of these *levels* if particles were

(a) spin 0 bosons;

(b) spin 1/2 fermions;

(c) spin 1 bosons.

solution

Levels	Energy	Degeneracy		
		Spin 0	Spin 1/2	Spin 1
(1,3)	10b	1	4	9
(2,2)	8b	1	1	6
(2,1)	5b	1	4	9
(1,1)	2b	1	1	6

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5. Two electrons occupy states ϕ_a and ϕ_b. Show that the slater determinant

$$\begin{vmatrix} \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) \\ \phi_b(1)\beta(1) & \phi_b(2)\beta(2) \end{vmatrix} \tag{1}$$

is not an eigenstate of $\mathbf{S}^2$ operator. Find the eigenstates of $\mathbf{S}^2$ operator by taking linear combinations of slater determinants.

solution

First we show that

$$\begin{aligned} &\mathbf{S}^2 \begin{vmatrix} \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) \\ \phi_b(1)\beta(1) & \phi_b(2)\beta(2) \end{vmatrix} \\ = \; &\hbar^2 \left(\begin{vmatrix} \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) \\ \phi_b(1)\beta(1) & \phi_b(2)\beta(2) \end{vmatrix} + \begin{vmatrix} \phi_a(1)\beta(1) & \phi_a(2)\beta(2) \\ \phi_b(1)\alpha(1) & \phi_b(2)\alpha(2) \end{vmatrix} \right) \end{aligned}$$

This gives us two $\mathbf{S}^2$ eigenfunctions

$$\begin{vmatrix} \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) \\ \phi_b(1)\beta(1) & \phi_b(2)\beta(2) \end{vmatrix} \pm \begin{vmatrix} \phi_a(1)\beta(1) & \phi_a(2)\beta(2) \\ \phi_b(1)\alpha(1) & \phi_b(2)\alpha(2) \end{vmatrix} \tag{2}$$

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6. Use variational function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi} \exp\left(-Z(r_1 + r_2)\right) \tag{3}$$

with Z as variational parameter to estimate the ground state energy of the Helium atom.

solution

Let the trial wave function be

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z_t^3}{\pi} \exp\left(-Z_t(r_1 + r_2)\right) \tag{4}$$

with Z_t as variational parameter. The Hamiltonian for helium can be rewritten as (in atomic units)

$$\begin{aligned}
\mathbf{H} &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_1} + \frac{1}{r_{12}} && (5)\\
&= \left(-\frac{1}{2}\nabla_1^2 - \frac{Z_t}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z_t}{r_2}\right) + \frac{Z_t - Z}{r_1} + \frac{Z_t - Z}{r_2} + \frac{1}{r_{12}} && (6)\\
&= \mathbf{h}_1 + \mathbf{h}_2 + \frac{Z_t - Z}{r_1} + \frac{Z_t - Z}{r_2} + \frac{1}{r_{12}} && (7)
\end{aligned}$$

Now,

$$\mathbf{h}_1\Psi = \mathbf{h}_1\Psi = -\frac{1}{2}Z_t^2\Psi \tag{8}$$

$$\left\langle \Psi \middle| \frac{1}{r_1}\Psi \right\rangle = \left\langle \Psi \middle| \frac{1}{r_2}\Psi \right\rangle = Z_t \tag{9}$$

$$\left\langle \Psi \middle| \frac{1}{r_{12}}\Psi \right\rangle = \frac{5}{8}Z_t \tag{10}$$

Thus, $E(Z_t) = Z_t^2 - 2Z\,Z_t + (5/8)Z_t$. Minimum energy is $-(Z - 5/16)^2$ atomic units (-77.46 eV). Minimum occurs at $Z_t = Z - 5/16$.