5.73

Quiz 30 ANSWERS

1.

The six np spin orbitals, listed in standard order, are: $1\alpha, 1\beta, 0\alpha, 0\beta, -1\alpha, -1\beta$.
The number $1, 0, -1$ refers to m_l, and α,β refers to $m_S = 1/2, -1/2$.

Matrix elements of a one-electron operator, $\mathbf{F} = \mathbf{f}(i)$, are

$\Delta so = 0\ \langle \| a_1 a_2 \| \mathbf{F} \| a_1 a_2 \| \rangle = \sum \langle a_i | \mathbf{f} | a_i \rangle$

$\Delta so = 0\ \langle \| a_1 b \| \mathbf{F} \| a_1 a_2 \| \rangle = \langle b_i | \mathbf{f} | a_2 \rangle$

$\langle p1 | \ell_+ | p0 \rangle = \langle p0 | \ell_+ | p-1 \rangle = 2^{1/2}$; $\langle \alpha | \mathbf{s}_+ | \beta \rangle = 1$

A. $\mathbf{F} \equiv \sum_i -\gamma B_z \left(\ell_{zi} + 2\mathbf{s}_{zi} \right)$. Evaluate $\langle \mathbf{F} \rangle$ for $\psi = \left\| 1\alpha 0\beta \right\|$.

This operator operates sequentially on electrons #1 and #2.

$$\left\langle \left\| 1\alpha 0\beta \right\| \sum_{i=1}^{2} -\gamma B_z \left(\ell_{zi} + 2s_{zi} \right) \left\| 1\alpha 0\beta \right\| \right\rangle$$

$$= -\gamma B_z \hbar \left[\underbrace{1+0}_{\ell_z} + \underbrace{2(1/2) + 2(-1/2)}_{s_z} \right] = -\gamma B_z \hbar$$

Recall $\ell_z \left| np\lambda \right\rangle = \hbar\lambda \left| np\lambda \right\rangle$.

B. $\mathbf{F} \equiv \mathbf{J}_+ = \sum_i \left(\ell_{+i} + \mathbf{s}_{+i} \right)$. Evaluate $\left\langle \left\| 1\alpha 0\alpha \right\| \mathbf{F} \left\| 1\alpha -1\alpha \right\| \right\rangle$.

[HINT: **F** is a sum, not a product, of two one-electron operators.]

There is an orbital mismatch in position #2. This is where we must put our $1e^-$ operator. This mismatch is "fixed" by ℓ_+ and NOT by $\mathbf{s}_+$.

$$\left\langle \left\| 1\alpha 0\alpha \right\| \sum_i \left(\ell_{+i} + \mathbf{s}_{+i} \right) \left\| 1\alpha -1\alpha \right\| \right\rangle = \left\langle 0\alpha \left| \ell_+ \right| -1\alpha \right\rangle$$

$$= \hbar \left[1\cdot 2 - (-1)\cdot 0 \right]^{1/2} = \sqrt{2}\hbar$$

C. $$\mathbf{F} = \sum_i \ell_i \cdot \mathbf{s}_i = \sum_i \left[\ell_{zi}\mathbf{s}_{zi} + \frac{1}{2}\left(\ell_{+i}\mathbf{s}_{-i} + \ell_{-i}\mathbf{s}_{+i} \right) \right].$$

Evaluate $\left\langle \left| 1\alpha 0\beta \right| \mathbf{F} \left| 1\alpha -1\alpha \right| \right\rangle$

The orbital mismatch is in position #2. It is "fixed" by 1/2 $\ell_+\mathbf{s}_-$.

$$\left\langle \left| 1\alpha 0\beta \right| \sum_i \left[\ell_{zi}\mathbf{s}_{zi} + \frac{1}{2}\left(\ell_{+i}\mathbf{s}_{-i} + \ell_{-i}\mathbf{s}_{+i} \right) \right] \left| 1\alpha -1\alpha \right| \right\rangle = \left\langle 0\beta \left| \frac{1}{2}\ell_+\mathbf{s}_- \right| -1\alpha \right\rangle$$

$$= \frac{1}{2}\hbar^2 \left[1\cdot 2 - (-1)\cdot 0 \right]^{1/2}$$

$$= 2^{-1/2}\hbar^2$$