Angular momentum, spin

Quantum Chemistry

Lesson 2

Contents

(Orbital) angular momentum

Classical mechanics

- $\vec{M} = \vec{r} \times \vec{p}\,, \quad \vec{M} = \sum_{K=1}^{N} \vec{r}_K \times \vec{p}_K$
- $M_i = \sum_{j,k=1}^{3} \varepsilon_{ijk} x_j p_k, \; \varepsilon_{ijk} = \mathrm{sign}[(j-i)(k-j)(k-i)], \ldots$

Quantum mechanics

- $\hat{\vec{X}} = [x, y, z], \quad \hat{\vec{P}} = [-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}]$
- $\hat{M}_x = -i\hbar y\frac{\partial}{\partial z} + i\hbar z\frac{\partial}{\partial y}\,, \hat{L}_x = \hat{M}_x/\hbar = -iy\frac{\partial}{\partial z} + iz\frac{\partial}{\partial y}$
- …

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Compatibility of angular momentum components

Commutation relations

- $\left[\hat{L}_j, \hat{L}_k\right] = i\varepsilon_{jkl}\hat{L}_l$
- angular momentum components are not compatible (only one of them can be measured)

Angular momentum magnitude

- $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$
- $\left[\hat{L}^2, \hat{L}_k\right] = 0$

Complete set of angular momentum observables

- $\hat{L}^2, \hat{L}_z$

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Angular momentum measurement

Spectrum $\hat{L}^2, \hat{L}_z$

- operators which commute share eigenvectors
  - $\hat{L}^2|L^2, L_z\rangle = L^2|L^2, L_z\rangle$
  - $\hat{L}_z|L^2, L_z\rangle = L_z|L^2, L_z\rangle$

Equations (*X*-representation)

- spherical coordinates ($x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$)
  - $\hat{L}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi}$
  - $\hat{L}_z = -i\frac{\partial}{\partial\phi}$
- $|L^2, L_z\rangle \to \varphi_{L^2L_z}(\theta,\phi)$ (*r* is missing, what does it mean?)
  - $-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\varphi_{L^2L_z}}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2\varphi_{L^2L_z}}{\partial^2\phi} = L^2\varphi_{L^2L_z}$
  - $-i\frac{\partial\varphi_{L^2L_z}}{\partial\phi} = L_z\varphi_{L^2L_z}$

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Angular momentum measurement

Solution

- eigenvalues
  - $L^2 = l(l+1), \quad l = 0, 1, 2, \ldots$
  - $L_z = m, \quad m = -l, -l+1, \ldots, l-1, l$

- eigenvectors (eigenfunctions)
  - $\varphi_{L^2 L_z}(\theta, \phi) = Y_{lm}(\theta, \phi)$
    - $Y_{lm}(\theta, \phi) \sim P_l^m(\cos\theta) e^{im\phi}$ [*spherical harmonics*]
    - $P_l^m(x) \sim (1 - x^2)^{m/2} \frac{\mathrm{d}^{m+l}}{\mathrm{d}x^{m+l}} (x^2 - 1)^l$ [*associated Legendre functions (of the second kind)*]

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Addition of (two) angular momenta

Two angular momenta (e.g., two particles) ...

- $\hat{\vec{L}}_1 \;\rightarrow\; \hat{L}_1^2, \hat{L}_{1z} \;\rightarrow\; |l_1, m_1\rangle, \quad Y_{l_1 m_1}(\theta_1, \phi_1)$
- $\hat{\vec{L}}_2 \;\rightarrow\; \hat{L}_2^2, \hat{L}_{2z} \;\rightarrow\; |l_2, m_2\rangle, \quad Y_{l_2 m_2}(\theta_2, \phi_2)$

... and their addition

- classical mechanics: $\vec{L}_1, \vec{L}_2 \rightarrow \vec{L} = \vec{L}_1 + \vec{L}_2$
- quantum mechanics: $\hat{\vec{L}}_1, \hat{\vec{L}}_2 \rightarrow \hat{\vec{L}} \quad = \hat{\vec{L}}_1 + \hat{\vec{L}}_2$

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Addition of (two) angular momenta

Picture 1 – two angular momenta

- $\hat{L}_1^2, \hat{L}_{1z}, \hat{L}_2^2, \hat{L}_{2z} \rightarrow |l_1, m_1\rangle |l_2, m_2\rangle = |l_1, m_1; l_2, m_2\rangle$ (tensor product of state spaces)
- X-representation: $|l_1, m_1; l_2, m_2\rangle = Y_{l_1 m_1}(\theta_1, \phi_1) Y_{l_2 m_2}(\theta_2, \phi_2)$

Picture 2 – total angular momentum

- $\hat{L}^2, \hat{L}_z \rightarrow |l, m\rangle$
  - $l = |l_1 - l_2|, \ldots, l_1 + l_2$
  - $m = -l, \ldots, +l$ (for each value of l)
- $|l, m\rangle$ = linear combinations of $|l_1, m_1; l_2, m_2\rangle$ (Clebsch-Gordan coefficients)

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Spin

Discovery

- experiment: space quantization of motion of silver atoms in inhomogeneous magnetic field (Gerlach, Stern 1922)
- theory: intrinsic angular momentum of the electron → intrinsic magnetic moment (Uhlenbeck, Goudsmit)

Spin properties

- no classical counterpart (the correspondence principle will not work)
- a kind of angular momentum → analogical behavior as that observed for the orbital angular momentum (dimensionless units)
  - magnitude: $S^2 = s(s+1)$
  - axis projection: $S_z = m_S,\ m_S = \xi = -s, -s+1, \ldots, s-1, s$
- electrons: $s = 1/2, \xi = \pm 1/2$

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Spin representation in quantum mechanics

State (one particle)

- $|\text{orbit}\rangle|\xi\rangle$, tensor product of orbital angular momentum and spin state spaces
- $\varphi(\vec{r},\xi) \;\rightarrow\;$ multicomponent wave functions (spinors): $\boldsymbol{\Psi}(\vec{r}) = \begin{bmatrix} \varphi(\vec{r},\xi=+s) \\ \vdots \\ \varphi(\vec{r},\xi=-s) \end{bmatrix} = \begin{bmatrix} \varphi_s(\vec{r}) \\ \vdots \\ \varphi_{-s}(\vec{r}) \end{bmatrix}$

Operators

- (hermitian) matrices $(2s+1)\times(2s+1)$
  - acting on spinor components
  - must obey the usual commutation relations of angular momentum operators: $[\hat{s}_j,\hat{s}_k] = i\varepsilon_{jkl}\hat{s}_l$
- for electrons (all the particles with $s=1/2$), e.g.,

$$\hat{s}_x = \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix},\quad \hat{s}_y = \begin{bmatrix} 0 & -i/2 \\ i/2 & 0 \end{bmatrix},\quad \hat{s}_z = \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$$

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Addition of spins

General rule (for adding any two angular momenta)

- the same procedure as that derived for the orbital angular momentum
- it means that the same rules can be used, e.g., for adding an orbital angular momentum and a spin

Example: Two electrons

- electrons
  - $s_1 = \frac{1}{2}, \quad \xi_1 = +\frac{1}{2}, -\frac{1}{2}$
  - $s_2 = \frac{1}{2}, \quad \xi_2 = +\frac{1}{2}, -\frac{1}{2}$
  - altogether 4 spin states
- total spin
  - $s = |s_1 - s_2|, \ldots, s_1 + s_2$; for each s: $\xi = -s, -s+1, \ldots, s-1, s$
    - $s = 0, \quad \xi = 0$
    - $s = 1, \quad \xi = +1, 0, -1$
  - altogether 1+3 = 4 spin states
  - *multiplicity*: (**singlet**, doublet, **triplet**, quadruplet, ... states for $s = \mathbf{0}, \frac{1}{2}, \mathbf{1}, \frac{3}{2}, \ldots$) a singlet and another triplet state

Addition of spins

Example: Three electrons

- 3 electrons
  - $s_1 = \frac{1}{2}, \xi_1 = +\frac{1}{2}, -\frac{1}{2};\ \ s_2 = \frac{1}{2}, \xi_2 = +\frac{1}{2}, -\frac{1}{2};\ \ s_3 = \frac{1}{2}, \xi_3 = +\frac{1}{2}, -\frac{1}{2}$
  - altogether 8 spin states
- a two-electron system and another electron added
  - $s_{12} = 0/1, \xi_{12} = 0/-1{,}0{,}1;\ \ s_3 = \frac{1}{2}, \xi_3 = +\frac{1}{2}, -\frac{1}{2}$
- total spin
  - $s = |s_{12} - s_3|, \dots, s_{12} + s_3;$ for each s: $\xi = -s, -s+1, \dots, s-1, s$
    - $s_{12} = 0 \ \rightarrow\ s = \frac{1}{2}, \quad \xi = +\frac{1}{2}, -\frac{1}{2}$
    - $s_{12} = 1 \ \rightarrow\ s = \frac{1}{2}, \quad \xi = +\frac{1}{2}, -\frac{1}{2}$
    - $\rightarrow\ s = \frac{3}{2}, \quad \xi = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
  - altogether 2+2+4 = 8 spin states
  - *multiplicity*: two doublet states and a quadruplet state

The end of lesson 2.