

MATH 728B, TRANSLATIONAL AND ROTATIONAL INVARIANCE

Suppose $A \in \text{SO}(3)$ is a rotation matrix and $\mathbf{b} \in \mathbb{R}^3$ is a translation vector. Together these determine a *rigid motion* which transforms $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ into $(A\mathbf{R}_1 + \mathbf{b}, \dots, A\mathbf{R}_M + \mathbf{b})$. Suppose ψ is a ground state electronic wavefunction “uniquely” determined by the requirements that its $\mathcal{H}(\mathbf{R}_1, \dots, \mathbf{R}_M)$ eigenvalue is $E = V(\mathbf{R}_1, \dots, \mathbf{R}_M)$, its \mathcal{S}^2 eigenvalue is $S(S + 1)\hbar^2$, and its \mathcal{S}_3 eigenvalue is $\hbar(S - \sigma)$ for some chosen integer $0 \leq \sigma \leq 2S$. What would be the corresponding electronic state for the molecule whose nuclei have been subjected to the rigid motion determined by (\mathbf{b}, A) ? If we could neglect the spin variables the answer would be $\tilde{\psi}(\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N) = \psi(A^T(\tilde{\mathbf{r}}_1 - \mathbf{b}), \dots, A^T(\tilde{\mathbf{r}}_N - \mathbf{b}))$. However, in order to obtain the corresponding electronic state for the rotated molecule we must reproduce its spin characteristics relative to a rotated apparatus for measuring spin related quantities. Thus we need to discuss spin in a little more detail.

If $s: \{0, 1\} \rightarrow \mathbb{C}$ is a function, then we can represent it using a column vector in \mathbb{C}^2 : $\begin{pmatrix} s(0) \\ s(1) \end{pmatrix}$. Let α_0 denote the function of this type represented by $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, and α_1 the function of this type represented by $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$. In quantum chemistry books α_0 and α_1 are usually called α and β , or *spin up* and *spin down*. This is because

$$\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Thus if α_0 is the spin state of a single electron then the value of the 3rd component of the spin (represented by the matrix $\hbar\sigma_3/2$) is $\hbar/2$. The ordered basis (α_0, α_1) is a basis of eigenvectors of the operator $\hbar\sigma_3/2$, called the *spin frame*. When the apparatus for measuring spin is rotated, then the spin frame is also rotated.

To understand the relation between rotations in \mathbb{R}^3 and rotations of the spin frame we introduce some notation. Define $X(\mathbf{x}) = \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3$, where σ_j , $j = 1, 2, 3$, are the Pauli spin matrices, and $\mathbf{x} = \langle x_1, x_2, x_3 \rangle = (x_1, x_2, x_3)^T$. $\frac{\hbar}{2}X(\mathbf{x})$ is the spin operator associated to measuring the spin (of a single electron) about an axis \mathbf{x} . Define $H(e^{i\theta}, \mathbf{u}) = \sigma_0 \cos \theta - iX(\mathbf{u}) \sin \theta$, where $\theta \in \mathbb{R}$ and $\mathbf{u} \in \mathbb{R}^3$ is a unit vector. Define also

$$R(e^{i\theta}, \mathbf{u}) = \mathbf{u}\mathbf{u}^T + (I - \mathbf{u}\mathbf{u}^T) \cos \theta + [\mathbf{u} \times] \sin \theta, \quad [\mathbf{u} \times] = \begin{pmatrix} 0 & -u_3 & u_2 \\ u_3 & 0 & -u_1 \\ -u_2 & u_1 & 0 \end{pmatrix},$$

where $\theta \in \mathbb{R}$ and $\mathbf{u} = \langle u_1, u_2, u_3 \rangle \in \mathbb{R}^3$ is a unit vector. The following result shows how to compute the spin operator about a rotated axis.

Fact. For all $\mathbf{x} \in \mathbb{R}^3$ we have $X(R(e^{i\theta}, \mathbf{u})\mathbf{x}) = H(e^{i\theta/2}, \mathbf{u})X(\mathbf{x})H(e^{i\theta/2}, \mathbf{u})^\dagger$, where H^\dagger is the complex conjugate transpose of the 2×2 complex matrix H .

The matrix $R(e^{i\theta}, \mathbf{u})$ is in the group $\text{SO}(3)$ of all rotation matrices, and represents the rotation about the axis \mathbf{u} through an angle θ (using the right-hand rule). The

matrix $H(e^{i\theta/2}, \mathbf{u})$ is in the group $SU(2)$ of all 2×2 complex matrices H such that $H^\dagger H = I$ and $\det H = 1$. Notice that the above fact allows us to define a mapping $SU(2) \rightarrow SO(3): H(e^{i\theta/2}, \mathbf{u}) \mapsto R(e^{i\theta}, \mathbf{u})$, but this mapping is not invertible. In fact both $H(e^{i\theta/2}, \mathbf{u})$ and $-H(e^{i\theta/2}, \mathbf{u}) = H(e^{i(\theta+2\pi)/2}, \mathbf{u})$ get mapped to the same $R(e^{i\theta}, \mathbf{u})$. *Technical comments for the mathematicians.* Both $SO(3)$ and $SU(2)$ are compact topological groups, and the mapping $SU(2) \rightarrow SO(3)$ is a continuous group homomorphism, which is a covering map. The group $SU(2)$ is simply connected whereas the fundamental group of $SO(3)$ is \mathbb{Z}_2 . Thus $SU(2)$ is the universal covering group of $SO(3)$. In fact $H(e^{i\theta/2}, \mathbf{u})$ can be identified with the homotopy class of the continuous path in $SO(3)$ connecting I with $R(e^{i\theta}, \mathbf{u})$, i.e. $[0, 1] \rightarrow SO(3): t \mapsto R(e^{it\theta}, \mathbf{u})$. The loop associated to $H(e^{i\pi}, \mathbf{u})$ can be taken as the (single) generator of the fundamental group of $SO(3)$, whereas the loop associated to $H(e^{i2\pi}, \mathbf{u}) = H(e^{i0}, \mathbf{u})$ is homotopic to the trivial loop (which remains at I for all $t \in [0, 1]$). (End of technical comments.)

The two column vectors $(H(e^{i\theta/2}, \mathbf{u})\alpha_0, H(e^{i\theta/2}, \mathbf{u})\alpha_1)$ of the matrix $H(e^{i\theta/2}, \mathbf{u})$ are the rotated spin frame if the rotation in \mathbb{R}^3 is given by $A = R(e^{i\theta}, \mathbf{u})$. For example, if we rotate molecule and the apparatus by $\theta = \pi/2$ about the y-axis $\mathbf{u} = \langle 0, 1, 0 \rangle$, then a measurement of the spin (of the original molecule) along the z-axis $\mathbf{x} = \langle 0, 0, 1 \rangle$ should correspond in the rotated molecule to a measurement of the spin along the x-axis $R(e^{i\pi/2}, \mathbf{u})\mathbf{x} = \langle 1, 0, 0 \rangle$. $X(\mathbf{x}) = \sigma_3$ and $X(R(e^{i\pi/2}, \mathbf{u})\mathbf{x}) = \sigma_1$. Then the above Fact becomes

$$\frac{\hbar}{2}\sigma_1 H(e^{i\pi/4}, \mathbf{u}) = H(e^{i\pi/4}, \mathbf{u}) \frac{\hbar}{2}\sigma_3,$$

i.e. the two column vectors of $H(e^{i\pi/4}, \mathbf{u})$ are the two eigenvectors of $\frac{\hbar}{2}\sigma_1$ with eigenvalues $\hbar/2$ and $-\hbar/2$ respectively. More generally, if we rotate the molecule and apparatus by θ about some axis \mathbf{u} perpendicular to $\mathbf{x} = \langle 0, 0, 1 \rangle$ then $\frac{\hbar}{2}X(R(e^{i\pi/2}, \mathbf{u})\mathbf{x})$ is the spin operator which is measured by the rotated apparatus, assuming originally it was set up to measure the z-component of spin: $\frac{\hbar}{2}X(\mathbf{x}) = \frac{\hbar}{2}\sigma_3$. The above Fact is then a restatement of the topic sentence of this paragraph. (End of example.) Thus if the spin characteristics of the original molecule are described by the spin function $s = \alpha_0 s(0) + \alpha_1 s(1)$, then the rotated molecule should have the spin characteristics contained in the function $H(e^{i\theta/2}, \mathbf{u})\alpha_0 s(0) + H(e^{i\theta/2}, \mathbf{u})\alpha_1 s(1)$, which is just the matrix $H(e^{i\theta/2}, \mathbf{u})$ multiplied by the column vector $\begin{pmatrix} s(0) \\ s(1) \end{pmatrix}$.

N -electron wavefunctions are functions of N spin variables; such functions can be thought of as tensors in $\mathbb{C}^2 \otimes \cdots \otimes \mathbb{C}^2$ (N times). If $s: \{0, 1\}^N \rightarrow \mathbb{C}$ is a spin function then we can always write

$$s = \sum_{\sigma_1=0}^1 \cdots \sum_{\sigma_N=0}^1 s(\sigma_1, \dots, \sigma_N) \alpha_{\sigma_1} \otimes \cdots \otimes \alpha_{\sigma_N},$$

where $(\gamma_1 \otimes \cdots \otimes \gamma_N)(\sigma'_1, \dots, \sigma'_N) = \gamma_1(\sigma'_1) \cdots \gamma_N(\sigma'_N)$, for all $(\sigma'_1, \dots, \sigma'_N) \in \{0, 1\}^N$, where $\gamma_j: \{0, 1\} \rightarrow \mathbb{C}$ are any functions, $j = 1, \dots, N$. If $U_j: \mathbb{C}^2 \rightarrow \mathbb{C}^2$ are linear transformations (i.e. 2×2 matrices), $j = 1, \dots, N$, then define the linear transformation $U_1 \otimes \cdots \otimes U_N: \mathbb{C}^2 \otimes \cdots \otimes \mathbb{C}^2 \rightarrow \mathbb{C}^2 \otimes \cdots \otimes \mathbb{C}^2$ by the rule: $(U_1 \otimes \cdots \otimes U_N)(\gamma_1 \otimes \cdots \otimes \gamma_N) = (U_1 \gamma_1) \otimes \cdots \otimes (U_N \gamma_N)$, extended by linearity. Recall we defined the operator $\mathcal{S}_k(j)$ to be

the matrix $\frac{\hbar}{2}\boldsymbol{\sigma}_k$ acting in the j th spin variable. In the above notation, this definition is expressed as

$$\mathcal{S}_k(j)s = \sum_{\sigma_1=0}^1 \cdots \sum_{\sigma_N=0}^1 s(\sigma_1, \dots, \sigma_N) \boldsymbol{\alpha}_{\sigma_1} \otimes \cdots \otimes \frac{\hbar}{2}\boldsymbol{\sigma}_k \boldsymbol{\alpha}_{\sigma_j} \otimes \cdots \otimes \boldsymbol{\alpha}_{\sigma_N},$$

i.e. $\mathcal{S}_k(j) = I \otimes \cdots \otimes \frac{\hbar}{2}\boldsymbol{\sigma}_k \otimes \cdots \otimes I$, where $\frac{\hbar}{2}\boldsymbol{\sigma}_k$ replaces the j th copy of I . Now we are prepared to state the following.

Lemma. *Suppose the spin function s is an eigenfunction of \mathcal{S}^2 with eigenvalue $\hbar^2 S(S+1)$ (where $S \in \{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots\}$) and is also an eigenfunction of \mathcal{S}_3 with eigenvalue $\hbar(S - \sigma)$ (where $0 \leq \sigma \leq 2S$). Define \tilde{s} by the rule:*

$$\tilde{s} = \sum_{\sigma_1=0}^1 \cdots \sum_{\sigma_N=0}^1 s(\sigma_1, \dots, \sigma_N) H(e^{i\theta/2}, \mathbf{u}) \boldsymbol{\alpha}_{\sigma_1} \otimes \cdots \otimes H(e^{i\theta/2}, \mathbf{u}) \boldsymbol{\alpha}_{\sigma_N},$$

where $\theta \in \mathbb{R}$ and $\mathbf{u} \in \mathbb{R}^3$ is a unit vector. If $\mathbf{x} = \langle 0, 0, 1 \rangle$ and $\mathbf{y} = R(e^{i\theta}, \mathbf{u})\mathbf{x} = \langle y_1, y_2, y_3 \rangle$ then define the rotated multi-electron spin operator by $\frac{\hbar}{2}\mathcal{X}(\mathbf{y}) = \mathcal{S}_1 y_1 + \mathcal{S}_2 y_2 + \mathcal{S}_3 y_3$, where $\mathcal{S}_k = \sum_{j=1}^N \mathcal{S}_k(j)$, $k = 1, 2, 3$. Then \tilde{s} is an eigenfunction of \mathcal{S}^2 with the same eigenvalue as s , and \tilde{s} is an eigenfunction of $\frac{\hbar}{2}\mathcal{X}(\mathbf{y})$ with eigenvalue $\hbar(S - \sigma)$.

Proof. See class notes.

Define $\mathfrak{h} = H(e^{i\theta/2}, \mathbf{u}) \otimes \cdots \otimes H(e^{i\theta/2}, \mathbf{u})$ (N times). Then the rotated and translated electronic wavefunction corresponding to ψ is $\tilde{\psi}$, defined by

$$\begin{aligned} & \tilde{\psi}(\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N, \tilde{\sigma}_1, \dots, \tilde{\sigma}_N) \\ &= \sum_{\sigma_1=0}^1 \cdots \sum_{\sigma_N=0}^1 \psi(A^T(\tilde{\mathbf{r}}_1 - \mathbf{b}), \dots, A^T(\tilde{\mathbf{r}}_N - \mathbf{b}), \sigma_1, \dots, \sigma_N) \cdot \\ & \quad \cdot \left\{ [H(e^{i\theta/2}, \mathbf{u}) \boldsymbol{\alpha}_{\sigma_1}] \otimes \cdots \otimes [H(e^{i\theta/2}, \mathbf{u}) \boldsymbol{\alpha}_{\sigma_N}] \right\} (\tilde{\sigma}_1, \dots, \tilde{\sigma}_N). \end{aligned}$$