Suppose $A \in \text{SO}(3)$ is a rotation matrix and $b \in \mathbb{R}^3$ is a translation vector. Together these determine a rigid motion which transforms $(R_1, \ldots, R_M)$ into $(AR_1 + b, \ldots, AR_M + b)$. Suppose $\psi$ is a ground state electronic wavefunction “uniquely” determined by the requirements that its $\mathcal{H}(R_1, \ldots, R_M)$ eigenvalue is $E = V(R_1, \ldots, R_M)$, its $S^2$ eigenvalue is $S(S+1)\hbar^2$, and its $S_3$ 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 $(b, A)$? If we could neglect the spin variables the answer would be $\tilde{\psi}(r_1, \ldots, r_N) = \psi(A^T (r_1 - b), \ldots, A^T (r_N - b))$. 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 $s : \{0, 1\} \to \mathbb{C}$ 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 $\alpha_0$ denote the function of this type represented by 
\[
\begin{pmatrix}
    1 \\
    0
\end{pmatrix},
\]
and $\alpha_1$ the function of this type represented by 
\[
\begin{pmatrix}
    0 \\
    1
\end{pmatrix}.
\]
In quantum chemistry books $\alpha_0$ and $\alpha_1$ are usually called $\alpha$ and $\beta$, or spin up and spin down. This is because 
\[
\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix},
\]
\[
\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\]
Thus if $\alpha_0$ 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 $(\alpha_0, \alpha_1)$ 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 
\[
X(x) = \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3,
\]
where $\sigma_j, \ j = 1, 2, 3,$ are the Pauli spin matrices, and $x = (x_1, x_2, x_3) = (x_1, x_2, x_3)^T$. $\frac{\hbar}{2} X(x)$ is the spin operator associated to measuring the spin (of a single electron) about an axis $x$. Define 
\[
H(e^{i\theta}, u) = \sigma_0 \cos \theta - iX(u) \sin \theta,
\]
where $\theta \in \mathbb{R}$ and $u \in \mathbb{R}^3$ is a unit vector. Define also 
\[
R(e^{i\theta}, u) = uu^T + (I - uu^T) \cos \theta + [u \times \sin \theta], \quad [u \times] = \begin{pmatrix}
    0 & -u_3 & u_2 \\
    u_3 & 0 & -u_1 \\
    -u_2 & u_1 & 0
\end{pmatrix},
\]
where $\theta \in \mathbb{R}$ and $u = (u_1, u_2, u_3) \in \mathbb{R}^3$ is a unit vector. The following result shows how to compute the spin operator about a rotated axis.

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

The matrix $R(e^{i\theta}, u)$ is in the group $\text{SO}(3)$ of all rotation matrices, and represents the rotation about the axis $u$ through an angle $\theta$ (using the right-hand rule).
matrix $H(e^{i\theta/2}, u)$ is in the group SU(2) of all $2 \times 2$ complex matrices $H$ such that $H^\dagger H = I$ and $\det H = 1$. Notice that the above fact allows us to define a mapping $SU(2) \to SO(3) : H(e^{i\theta/2}, u) \mapsto R(e^{i\theta}, u)$, but this mapping is not invertible. In fact both $H(e^{i\theta/2}, u)$ and $-H(e^{i\theta/2}, u) = H(e^{i(\theta+2\pi)/2}, u)$ get mapped to the same $R(e^{i\theta}, u)$. Technical comments for the mathematicians. Both SO(3) and SU(2) are compact topological groups, and the mapping $SU(2) \to SO(3)$ 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 $H(e^{i\theta/2}, u)$ can be identified with the homotopy class of the continuous path in SO(3) connecting $I$ with $R(e^{i\theta}, u)$, i.e. $[0, 1] \to SO(3) : t \mapsto R(e^{it\theta}, u)$. The loop associated to $H(e^{i\pi}, u)$ can be taken as the (single) generator of the fundamental group of SO(3), whereas the loop associated to $H(e^{i\pi/2}, u) = H(e^{i\theta}, u)$ is homotopic to the trivial loop (which remains at $I$ for all $t \in [0, 1]$). (End of technical comments.)

The two column vectors $(H(e^{i\theta/2}, u)\mathbf{a}_0, H(e^{i\theta/2}, u)\mathbf{a}_1)$ of the matrix $H(e^{i\theta/2}, u)$ are the rotated spin frame if the rotation in $\mathbb{R}^3$ is given by $A = R(e^{i\theta}, u)$. For example, if we rotate molecule and the apparatus by $\theta = \pi/2$ about the y-axis $u = \langle 0, 1, 0 \rangle$, then a measurement of the spin (of the original molecule) along the z-axis $x = \langle 0, 0, 1 \rangle$ should correspond in the rotated molecule to a measurement of the spin along the x-axis $R(e^{i\pi/2}, u)x = \langle 1, 0, 0 \rangle$.

$X(x) = \mathbf{\sigma}_3$ and $X(R(e^{i\pi/2}, u)x) = \mathbf{\sigma}_1$. Then the above Fact becomes

$$\frac{\hbar}{2} \mathbf{\sigma}_1 H(e^{i\pi/4}, u) = H(e^{i\pi/4}, u) \frac{\hbar}{2} \mathbf{\sigma}_3,$$

i.e. the two column vectors of $H(e^{i\pi/4}, u)$ are the two eigenvectors of $\frac{\hbar}{2} \mathbf{\sigma}_1$ with eigenvalues $\hbar/2$ and $-\hbar/2$ respectively. More generally, if we rotate the molecule and apparatus by $\theta$ about some axis $u$ perpendicular to $x = \langle 0, 0, 1 \rangle$ then $\frac{\hbar}{2} X(R(e^{i\pi/2}, u)x)$ is the spin operator which is measured by the rotated apparatus, assuming originally it was set up to measure the z-component of spin: $\frac{\hbar}{2} X(x) = \frac{\hbar}{2} \mathbf{\sigma}_3$. 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 $s = \mathbf{a}_0 s(0) + \mathbf{a}_1 s(1)$, then the rotated molecule should have the spin characteristics contained in the function $H(e^{i\theta/2}, u)\mathbf{a}_0 s(0) + H(e^{i\theta/2}, u)\mathbf{a}_1 s(1)$, which is just the matrix $H(e^{i\theta/2}, u)$ 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 $s : \{0, 1\}^N \to \mathbb{C}$ is a spin function then we can always write

$$s = \sum_{\sigma_1 = 0} \cdots \sum_{\sigma_N = 0} s(\sigma_1, \ldots, \sigma_N) \mathbf{a}_{\sigma_1} \otimes \cdots \otimes \mathbf{a}_{\sigma_N},$$

where $(\gamma_1 \otimes \cdots \otimes \gamma_N)(\sigma'_1, \ldots, \sigma'_N) = \gamma_1(\sigma'_1) \cdots \gamma_N(\sigma'_N)$, for all $(\sigma'_1, \ldots, \sigma'_N) \in \{0, 1\}^N$, where $\gamma_j : \{0, 1\} \to \mathbb{C}$ are any functions, $j = 1, \ldots, N$. If $U_j : \mathbb{C}^2 \to \mathbb{C}^2$ are linear transformations (i.e. $2 \times 2$ matrices), $j = 1, \ldots, N$, then define the linear transformation $U_1 \otimes \cdots \otimes U_N : \mathbb{C}^2 \otimes \cdots \otimes \mathbb{C}^2 \to \mathbb{C}^2 \otimes \cdots \otimes \mathbb{C}^2$ 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 $S_k(j)$ to be
the matrix \( \frac{\hbar}{2} \sigma_k \) acting in the \( j \)th spin variable. In the above notation, this definition is expressed as

\[
S_k(j)s = \sum_{\sigma_1 = 0}^{1} \cdots \sum_{\sigma_N = 0}^{1} s(\sigma_1, \ldots, \sigma_N) \alpha_{\sigma_1} \otimes \cdots \otimes \frac{\hbar}{2} \sigma_k \alpha_{\sigma_j} \otimes \cdots \otimes \alpha_{\sigma_N},
\]

i.e. \( S_k(j) = I \otimes \cdots \otimes \frac{\hbar}{2} \sigma_k \otimes \cdots \otimes I \), where \( \frac{\hbar}{2} \sigma_k \) 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 \( S^2 \) with eigenvalue \( \hbar^2 S(S+1) \) (where \( S \in \{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots \} \)) and is also an eigenfunction of \( S_3 \) with eigenvalue \( \hbar(S-\sigma) \) (where \( 0 \leq \sigma \leq 2S \)). Define \( \tilde{s} \) by the rule:

\[
\tilde{s} = \sum_{\sigma_1 = 0}^{1} \cdots \sum_{\sigma_N = 0}^{1} s(\sigma_1, \ldots, \sigma_N) H(e^{i\theta/2}, u) \alpha_{\sigma_1} \otimes \cdots \otimes H(e^{i\theta/2}, u) \alpha_{\sigma_N},
\]

where \( \theta \in \mathbb{R} \) and \( u \in \mathbb{R}^3 \) is a unit vector. If \( x = (0, 0, 1) \) and \( y = R(e^{i\theta}, u)x = (y_1, y_2, y_3) \) then define the rotated multi-electron spin operator by \( \frac{\hbar}{2} X(y) = S_1y_1 + S_2y_2 + S_3y_3 \), where \( S_k = \sum_{j=1}^{N} S_k(j), k = 1, 2, 3 \). Then \( \tilde{s} \) is an eigenfunction of \( S^2 \) with the same eigenvalue as \( s \), and \( \tilde{s} \) is an eigenfunction of \( \frac{\hbar}{2} X(y) \) with eigenvalue \( \hbar(S-\sigma) \).

**Proof.** See class notes.

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

\[
\tilde{\psi}(\tilde{r}_1, \ldots, \tilde{r}_N, \tilde{\sigma}_1, \ldots, \tilde{\sigma}_N) = \sum_{\sigma_1 = 0}^{1} \cdots \sum_{\sigma_N = 0}^{1} \psi(A^T(\tilde{r}_1 - b), \ldots, A^T(\tilde{r}_N - b), \sigma_1, \ldots, \sigma_N) \cdot \left\{ [H(e^{i\theta/2}, u)\alpha_{\sigma_1}] \otimes \cdots \otimes [H(e^{i\theta/2}, u)\alpha_{\sigma_N}] \right\}(\tilde{\sigma}_1, \ldots, \tilde{\sigma}_N).
\]