Example exam CTC2, NWI-MOL176

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- Put your **name**, student number, and date **on every page**. Also number your pages.
- You can bring one, double sided (printed) page with equations to the exam.
- Include your scratch paper.

Question 1: Spin-orbit coupling in the NH radical

The NH radical has a triplet ground state, i.e., the electronic spin quantum number is $S = 1$. In the lecture we did not discuss electronic spin, but in the questions you can use that the commutation relations for the electron spin operators, $\hat{\boldsymbol{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$, are exactly the same as for the orbital angular momentum operators $\hat{\boldsymbol{l}} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$. The electron spin functions are denoted as $|S, M_S\rangle$, analogous to the $|lm\rangle$ angular momentum functions. The projection quantum numbers M_S and m correspond to the same "space-fixed" z-axis.

The Hamiltonian ($\hat{H}$) for NH, neglecting vibration, is given by

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{SO}},$$

with rotational Hamiltonian (with rotational constant B),

$$\hat{H}_{\text{rot}} = B\hat{l}^2,$$

and spin-orbit coupling

$$\hat{H}_{\text{SO}} = A\hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{S}},$$

where A is the spin-orbit coupling constant. The solutions Ψ_i with energy E_i of the Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i$$

can be expanded in an "uncoupled basis" as

$$\Psi_i = \sum_{lmM_S} |lm\rangle|SM_S\rangle c_{lmSM_S;i},$$

where $c_{lmSM_S;i}$ are the expansion coefficients.

1a. Give the matrix elements of rotational Hamiltonian in the uncoupled basis, and give the possible values of all quantum numbers.

1b. Derive the matrix elements of the spin-orbit Hamiltonian in the uncoupled basis.

1c. Which of quantum numbers l, m, S, and M_S are *good quantum numbers* ? Briefly explain your answer.

The Hamiltonian $\hat{H}$ is invariant under rotation. This makes it possible to define a new basis with additional good quantum numbers.

1d. Define such a basis and give all good quantum numbers for this basis. Also give the possible values for the quantum numbers in this basis.

If the molecule is put in a magnetic field along the x-axis, it is more convenient to express the wave function in a basis where the projection quantum numbers refer to the projection of the angular momentum on the y-axis, rather than the z-axis. Thus, we define new angular momentum states,

$$|lmSM_S\rangle^{(x)} = \hat{R}\ (|lm\rangle|SM_S\rangle)\,.$$

1e. Give the expression for the rotation operator $\hat{R}$ that rotates the (rotational) wave function around the y-axis, such that in the states $|lmSM_S\rangle^{(x)}$ the projection of the angular momentum on the x-axis is $\hbar m$ and give the matrix elements of $\hat{R}$ in the space-fixed basis with functions $|lmSM_S\rangle$.

Question 2: Parity in body-fixed coordinates

Consider an atom-diatom (A−BC) system in Jacobi coordinates $(\boldsymbol{r}, \boldsymbol{R})$, where

$$\boldsymbol{r} \equiv \boldsymbol{r}_{\mathrm{B}} - \boldsymbol{r}_{\mathrm{C}}$$
$$\boldsymbol{R} \equiv \boldsymbol{r}_{\mathrm{A}} - \boldsymbol{r}_{\mathrm{BC}}$$

and $\boldsymbol{r}_{\mathrm{BC}}$ is the center-of-mass of molecule BC. The inversion operator $\hat{\imath}$ acts on the atomic coordinates $\boldsymbol{r}_{\mathrm{X}}$ with X = A, B, or C as

$$\hat{\imath}\boldsymbol{r}_{\mathrm{X}} = -\boldsymbol{r}_{\mathrm{X}}.$$

2a. Derive the action of $\hat{\imath}$ on the Jacobi coordinates $\boldsymbol{r}$ and $\boldsymbol{R}$ (give all steps of the derivation).

We define a new "body-fixed" coordinate frame, with the z-axis $\boldsymbol{b}_z$ along the Jacobi vector,

$$\boldsymbol{b}_z \equiv \frac{1}{R}\boldsymbol{R}, \quad (\text{with } R = |\boldsymbol{R}|).$$

The x-axis of the body-fixed frame is define by the cross product

$$\boldsymbol{b}_x \equiv |N|\, \boldsymbol{e}_z \times \boldsymbol{b}_z,$$

where N normalizes the vector $\boldsymbol{b}_x$, and $\boldsymbol{e}_z$ is the space-fixed z-axis

$$\boldsymbol{e}_z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

Finally, the body-fixed y axis is defined by

$$\boldsymbol{b}_y = \boldsymbol{b}_z \times \boldsymbol{b}_x,$$

such that the matrix

$$\boldsymbol{B} = [\boldsymbol{b}_x \boldsymbol{b}_y \boldsymbol{b}_z]$$

defines a right-handed orthonormal frame.

2b. Derive the action of the inversion operator $\hat{\imath}$ onto the body-fixed frame $\boldsymbol{B}$.

The diatomic coordinate $\boldsymbol{r}$ can be expressed in the body-fixed frame by

$$\boldsymbol{r} = \boldsymbol{B}\boldsymbol{r}^{(\mathrm{BF})}.$$

2c. Using the action of the inversion operator $\hat{\imath}$ on the vectors $\boldsymbol{r}$ and the columns of the matrix $\boldsymbol{B}$, derive the action of $\hat{\imath}$ on the three components of the body-fixed vector $\boldsymbol{r}^{(\mathrm{B})}$

2d. Give the matrix-representation of the inversion operator $\hat{\imath}$ in the body-fixed frame $\boldsymbol{B}$, and show that the matrix corresponds to a reflection and give the reflection plane.

Question 3: The HF molecule in an electric field

The interaction of HF, which has an electric dipole moment of $\mu = 0.7\ ea_0$, with an electric field of strength E along the space-fixed z-axis is given by the Stark Hamiltonian

$$\hat{H}_{\text{Stark}} = -E\mu\cos(\theta),$$

where θ is the angle between the molecular axis and the space-fixed z-axis. Here we consider the molecule HF with rotational states $|lm\rangle$.

3a. Derive an expression for the matrix elements of the Stark Hamiltonian in the rotational basis $|lm\rangle$,

$$H_{l'm';lm} = \langle l'm'|\hat{H}_{\text{Stark}}|lm\rangle.$$

3b. Give the selection rules for these matrix elements, i.e., for which combinations of the quantum numbers l', m', l, and m are the matrix elements equal to zero?

The Hamiltonian that describes the rotation of HF (with dipole moment μ) in an electric field (of strength E), is given by

$$\hat{H} = B\hat{l}^2 + \hat{H}_{\text{Stark}}.$$

3c. Write down the time-dependent Schrödinger equation for this system and give the matrix elements of $\hat{H}$ in the rotational basis.

Consider a molecule that is in $l = 0$ at time $t = 0$. For simplicity, we only consider the coupling by the electric field of the initial state to the rotational state $|l, m\rangle = |1, 0\rangle$.

3d. Solve the time-dependent Schrödinger equation, and give the probability $P(t)$ of observing the molecule in the $l = 1$ state at times $t > 0$.