

Example exam CTC2, NWI-MOL176

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- Put your **name**, student number, and date **on every page**. Also number your pages.
- A printed version of the **lecture notes can be used** during 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, $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$, are exactly the same as for the orbital angular momentum operators $\hat{\mathbf{l}} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$. 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

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

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 (\mathbf{r}, \mathbf{R}) , where

$$\begin{aligned}\mathbf{r} &\equiv \mathbf{r}_B - \mathbf{r}_C \\ \mathbf{R} &\equiv \mathbf{r}_A - \mathbf{r}_{BC}\end{aligned}$$

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

$$\hat{i}\mathbf{r}_X = -\mathbf{r}_X.$$

- 2a.** Derive the action of \hat{i} on the Jacobi coordinates \mathbf{r} and \mathbf{R} (give all steps of the derivation).

We define a new “body-fixed” coordinate frame, with the z -axis \mathbf{b}_z along the Jacobi vector,

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

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

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

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

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

Finally, the body-fixed y axis is defined by

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

such that the matrix

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

defines a right-handed orthonormal frame.

- 2b.** Derive the action of the inversion operator \hat{i} onto the body-fixed frame \mathbf{B} .

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

$$\mathbf{r} = \mathbf{B}\mathbf{r}^{(\text{BF})}.$$

- 2c.** Using the action of the inversion operator \hat{i} on the vectors \mathbf{r} and the columns of the matrix \mathbf{B} , derive the action of \hat{i} on the three components of the body-fixed vector $\mathbf{r}^{(\text{B})}$
- 2d.** Give the matrix-representation of the inversion operator \hat{i} in the body-fixed frame \mathbf{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 $t > 0$.