1. Convince yourself of the effects of the SO(4) symmetry of the hydrogen atom (see lecture) [6 points]

The (non-relativistic) Hamiltonian for the hydrogen atom is (in atomic units)

\[ H = -\frac{1}{2} \nabla^2 - \frac{1}{r}. \]

The associated eigenvalue problem reads

\[ H \Psi_{nlm} = E \Psi_{nlm}, \]

with \( E = -\frac{1}{2} n^2 \), where \( n \) is the principal quantum number, and the degeneration of \( E \) is \( n^2 \).

We define the renormalized Runge-Lenz vector

\[ M = \frac{1}{\sqrt{-2E}} \left[ \frac{1}{2} (p \times L - L \times p) - \frac{r}{r} \right]. \]

The operator \( L \) is the angular momentum, and \( L^2 \Psi_{nlm} = l(l+1)\Psi_{nlm} \), with \( l = 0, 1, \ldots n - 1 \). In short we write the last relation as \( L^2 = l(l+1) \).

The commutation relations of \( L \), \( M \), and the Hamiltonian are \([H, L_i] = [H, M_i] = 0\), where \( i = x, y, z \); \([L_x, L_y] = iL_z \) (and cyclic); \([L_x, M_y] = iM_z \) (and cyclic); \([M_x, M_y] = iL_z \) (and cyclic).

Furthermore the following relation holds: \( M^2 = -\frac{1}{2E} - (L^2 + 1) \).

Following what we have done in class, show that

- \( L \cdot M = 0 = M \cdot L \)
- \( J_1 = (L + M)/2 \) and \( J_2 = (L - M)/2 \) build two commuting set of operators each satisfying the commutation relations of ordinary angular momentum. Hence \( J_1^2 = j_1(j_1 + 1) \) and \( J_2^2 = j_2(j_2 + 1) \)
- \( J_1^2 = J_2^2 \), hence \( j_1 = j_2 = j \)
- \( E = -\frac{1}{2} \frac{1}{(2j+1)} \), and hence \( 2j + 1 = n \).
- the possible values of \( l \) are \( l = 0, 1, 2, \ldots, 2j \) (Hint: use the addition of angular momentum).
- the degeneracy of the eigenvalue is \( \sum_{0}^{2j} (2l+1) = (2j+1)^2 \equiv n^2 \)

2. Crystal-field in Graphene [4 points]

Graphene (Nobel Prize 2010) is a two-dimensional material made of C regular hexagons. The symmetry of a C site for an ideal monolayer graphene
on an isotropic medium is $D_{3h} = D_3 \otimes C_{1h}$. The character table of $D_{3h}$ is given below.

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C'_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A'_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Using the decomposition formula, calculate how the $p$ levels $(x, y, z)$ of C split in graphene, i.e., decompose the $\Gamma^p$ reducible representation into irreducible representations of $D_{3h}$. Assume that one of the C atoms is replaced by a transition-metal impurity, e.g., a Ti atom. How do the $d$ level of the Ti atom split? Decompose the $\Gamma^d$ reducible representation into irreducible representations of $D_{3h}$. Construct two invariant functions.

3. Point group of various molecules [4 points]
Using the procedure explained in the lecture, in particular the slide “assign a point group”, identify the point symmetry group of the molecules in the next page. Start from identifying the principal axis. Explain for each molecule the reasons of your conclusion.
Abbildung 1: Various small molecules