

Ligand-Field Theory

- Ligands can be ordered in increasing “field strength”: the *spectrochemical series*.
- Weak field ligands such as the halides favour high-spin states, whereas ligands like CN^- favour low-spin states.
- Across a series of ligands the ground state may change: the energy behaviour with ligand strength can be plotted on a type of correlation diagram (Tanabe-Sugano diagram).
- Where spin-orbit coupling is strong, this will have to be taken care of first.
- We will look at the behaviour of electronic states under perturbations again later.



Molecular properties

- Suppose we have some perturbation of the system measured by a strength parameter λ .
- We can expand the energy in a Maclaurin expansion

$$E = E_0 + \left. \frac{dE}{d\lambda} \right|_{\lambda=0} \lambda + \frac{1}{2} \left. \frac{d^2 E}{d\lambda^2} \right|_{\lambda=0} \lambda^2 + \dots$$

- The derivatives correspond to the first-order, second-order, etc., response of the system to the applied perturbation.
- These are termed first-order properties, etc. For example, if λ measures the strength of an applied homogeneous electric field along the z -axis, $dE/d\lambda|_{\lambda=0}$ corresponds to the z component of the dipole moment.



Properties as Energy Derivatives

- More elaborately, we can imagine a *vector* of applied perturbations \vec{F} and the expansion

$$E = E_0 + \sum_i \left. \frac{dE}{dF_i} \right|_{\vec{F}=0} F_i + \frac{1}{2} \sum_{ij} \left. \frac{d^2 E}{dF_i dF_j} \right|_{\vec{F}=0} F_i F_j \dots$$

- Express properties as derivatives of the energy with respect to these perturbations. E.g., harmonic force constants are second derivatives with respect to displacing the nuclei; the dipole moment vector is the first derivative with respect to an applied electric field.
- What do we learn from group theory about these properties?



Symmetry and Properties

- The energy is a scalar function of the perturbation. Hence in order to be nonvanishing any energy derivative must transform as a basis function for the totally symmetric irrep.
- This means that for a first-order property described by dE/dF_i , F_i must be a basis function for the totally symmetric irrep.
- For a second-order property $d^2E/dF_i dF_j$ this means that the representation $\Gamma(F_i) \otimes \Gamma(F_j)$ must contain the totally symmetric irrep, etc.
- Let us look at some particular cases in practice.



Symmetry and Properties

- Suppose the perturbation is a static homogeneous electric field. This would be described by a vector of field strengths (f_x, f_y, f_z) .
- For the molecule to have a nonvanishing dipole moment μ_i in direction i , the field component f_i must transform as a basis function for the totally symmetric irrep.
- For NH_3 (C_{3v}) this means that μ_z *may* be nonzero, whereas the other two components are zero by symmetry.
- What about second-order properties with respect to an applied field.



Symmetry and Properties

- The second derivative with respect to components of a static homogeneous electric field is an element of the *polarizability tensor* α .
- For the molecule to have a nonvanishing polarizability component α_{ij} in directions i and j , the product representation $\Gamma(f_i) \otimes \Gamma(f_j)$ must contain the totally symmetric irrep. This implies $\Gamma(f_i) = \Gamma(f_j)$
- Sidebar: NH_3 polarizability.
- Note that all these results are specific to the orientation of the molecule.



Symmetry of Nuclear Motion

- The perturbation is movement of the nuclei in the molecule.
- The Cartesian coordinates of all nuclei in the molecule form a basis for a (generally reducible) representation of the point group.
- For example, for NH_3 (C_{3v}) the Cartesian coordinates of N transform as $A_1 + E$, while those of the three H's together transform as $2A_1 + A_2 + 3E$.
- This in itself is only part of what we need.
- In the absence of external fields, the energy of the molecule is invariant to translations and rotations.



Elimination of Translation and Rotation

- The irreps spanned by rotation and translation are those for which a simple axial vector and a polar vector respectively form a basis.
- These irreps are usually listed in character tables.
- For example, for NH_3 (C_{3v}) rotations transform as a basis for $A_2 + E$ and translations transform as a basis for $A_1 + E$.
- The remaining $3n - 6$ nuclear motions are of course vibrations, which transform here as $2A_1 + 2E$.
- For linear molecules there are only two rotational modes and $3n - 7$ vibrations.



Nuclear Motion Properties

- The first derivative of the energy with respect to nuclear motion is the energy gradient.
- Only totally symmetric elements of the gradient are nonvanishing. And the gradient with respect to rotations and translations is also zero in the absence of external fields.
- This is only obvious for certain choices of coordinates.
- Sidebar: coordinates in NH_3 .



Nuclear Motion Properties

- Second derivatives with respect to nuclear motion are harmonic force constants.
- There are $(3n - 6) \times (3n - 6)$ force constants that remain after elimination of rotation and translation.
- The nonvanishing force constants F_{ij} must satisfy $\Gamma(i) = \Gamma(j)$.
- Hence the force constant matrix is block-diagonal on irreps. In fact, it is block-diagonal on symmetry species.

