X_3 molecule – the E x e Jahn-Teller problem
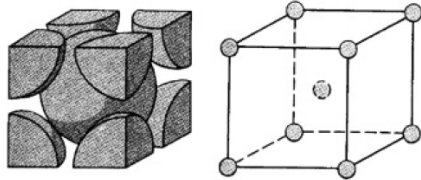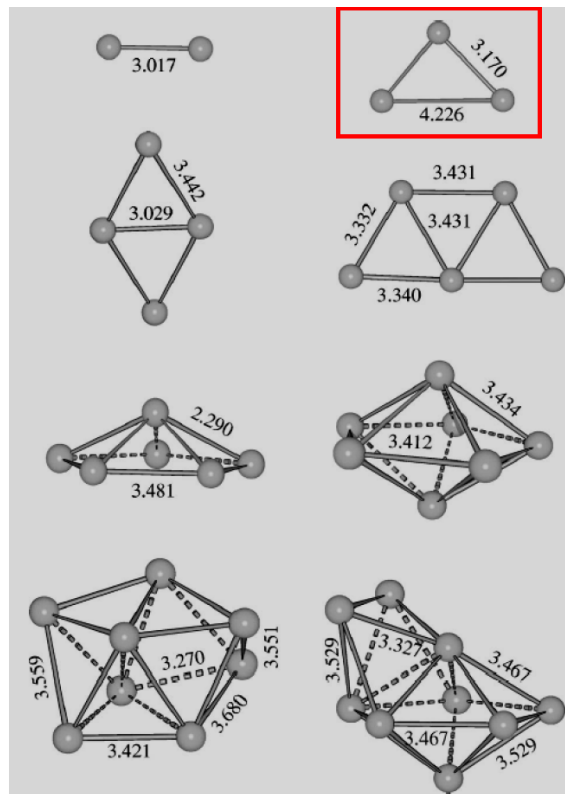
"Static polarizabilities of Na_n ($n < 10$) clusters: An all-electron density functional study"
P. Calaminici, K. Jug, and A. M. Köster,
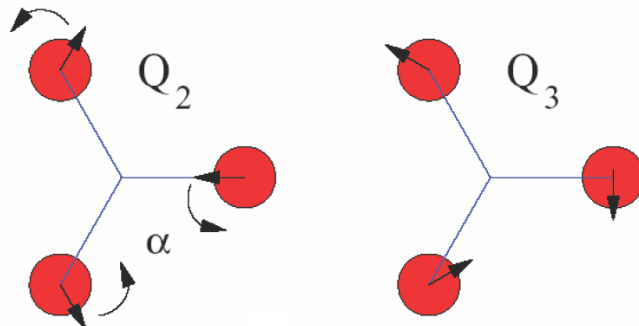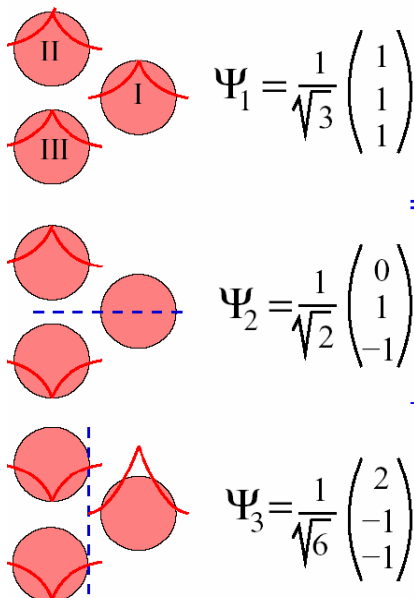J. Chem. Phys. 111, 4613 (1999).

Bulk sodium, bcc
d=3.66 Angstroms

Clusters of atoms of various kinds have been a popular topic of investigation. The trimer Na_3 serves as a realization of the X3 molecule discussed by Longuet-Higgins. In its simplest equilateral triangle form, the Huckel Hamiltonian for electron orbitals is shown below, and eigenstates are pictured below it. We also want to look at vibrations.

$$\mathcal{H}_0 = -t \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

There are 3N-6=3 vibrational normal modes. The group is D_{3h}. There is a "breathing mode" of A_1 symmetry. There is a E doublet, shown below. The

$$\Psi_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

$$\Psi_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$$

$$\Psi_3 = \frac{1}{\sqrt{6}} \begin{pmatrix} 2 \\ -1 \\ -1 \end{pmatrix}$$

symbols Q_2 and Q_3 are Van Vleck's notation for the amplitudes of the components of the E doublet. Electron eigenstates also have an A1 singlet and an E doublet. Pictures of the wavefunctions are shown on

the left. The 3-vector notation gives amplitudes of the atomic orbitals on atoms I, II, III.

Below on the left is the charge density of the distorted ground state; on the right is the HOMO wavefunction of the distorted ground state. Notice the nodal plane. It is a B_2 state of the C_{2v} point group. These are from Martins, Buttet, and Car, Phys. Rev. B **31**, 1804 (1985); J. Chem. Phys. **78**, 5646 (1983)
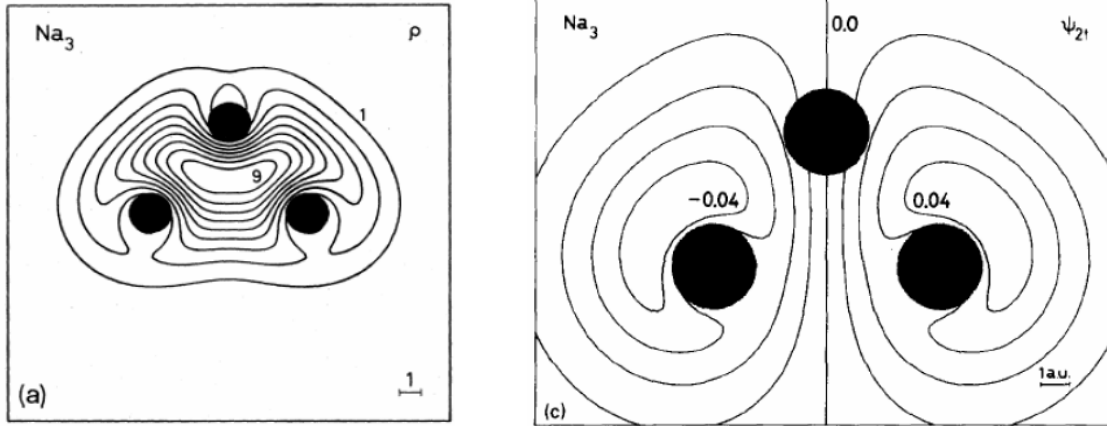
The Hamiltonian for electrons in Huckel approximation is $\mathcal{H} = \Sigma_{<ij>}(-t + \boxed{g\delta R_{ij}})c_i^\dagger c_j = \mathcal{H}_t + \boxed{\mathcal{H}_{ep}}$
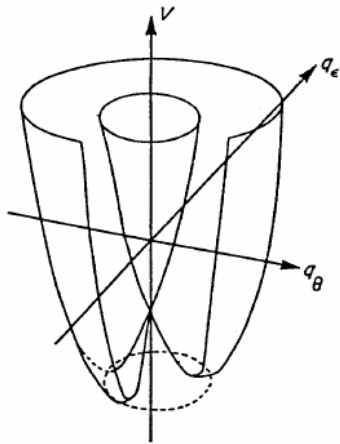This is sometimes called "Su-Schrieffer-Heeger coupling, after their model for polyacetylene $(CH)_x$. Now truncate the Hamiltonian to the subspace of the E doublet.

$$|\Psi> = c_2|\Psi_2> + c_3|\Psi_3> = \begin{pmatrix} c_2 \\ c_3 \end{pmatrix}$$

$$\boxed{\mathcal{H}_{ep}} = gQ \begin{pmatrix} -\cos\alpha & \sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix}$$

eigenvalues $\pm g|Q|$

groundstate $\begin{pmatrix} \sin(\alpha/2) \\ \cos(\alpha/2) \end{pmatrix}$

The angle α (known as the angle of "pseudo-rotation") describes the orientation of the vibrational displacement in the abstract Q_2,Q_3 space. It is $\cos\alpha$ times a Q_2 displacement plus $\sin\alpha$ times a Q_3. The energy splitting is independent of the angle α. The total energy is then a harmonic restoring force

$$(1/2)K(Q_1^2 + Q_2^2) = (1/2)KQ^2,$$

plus the energy lowering $-gQ$ from the Jahn-Teller splitting. This is the "Mexican hat" potential shown to the left. The axes should be relabeled Q_2 and Q_3. 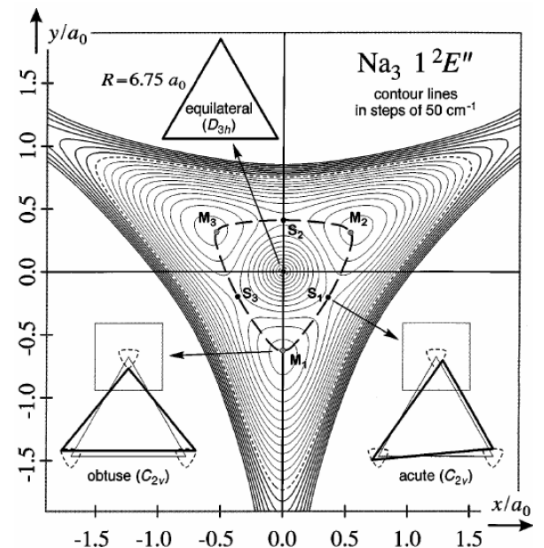On the right is a density functional calculation showing that the true potential is warped and has three equivalent minima (H. von Busch, V. Dev, H. A. Eckel, et al. *Unambiguous proof for Berry's phase in the sodium trimer*, PRL 81, 4584 (1998).)

The pseudo-rotation is a funny kind of motion, where each X atom rotates around the undistorted position, in such a way that the center of mass of the three X atoms is fixed. This rotation actually does carry real angular momentum. As the pseudo-rotation completes one 2π cycle, the lower occupied (and also the upper unoccupied) Jahn-Teller-split states change sign (have a Berry phase of π.) This trick of mathematics is actually quite a physical effect. You can convince yourself of it physically by studying the diagram on the right. The line of nodes rotates reverse to α, and half as fast.

The vibrational problem is governed by the 2 degree of freedom Hamiltonian shown below.

$$\mathcal{H}_{\text{dist}} = \left(\frac{P_q^2}{6M} + \frac{L_\alpha^2}{6Mq^2} \right) + \frac{9}{4}Kq^2 - \sqrt{3}gq$$
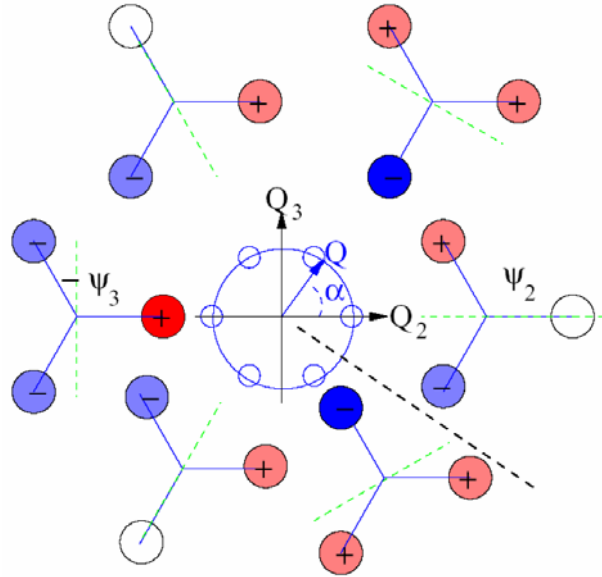
Here L_α is the pseudo-angular momentum operator. The solution of the angular part is free 2-d pseudo-rotation.

The wavefunctions are shown on the right. The total wavefunction is single-valued. But the electron part of the wavefunction changes sign on a complete pseudo-rotation. In order to make the total wavefunction single-

$$\Psi_{\text{dist}} = e^{im\alpha}\psi_{\text{vib}}(q)$$
$$\Psi_{\text{tot}} = \Psi_{\text{dist}}\Psi_{\text{el}}$$

valued, it is necessary to compensate for this sign change by forcing the pseudo-angular-momentum quantum number m to be half integral. So the Berry phase has a real physical consequence, as first noticed by Longuet-Higgins.

Real molecules are quite a bit more complicated. The 3-d rotations of an asymmetric top molecule need to be included, and further alter the physics. In addition, the nuclei are identical but may have non-zero spin (Na nuclei have spin 3/2.) Proper symmetry under nuclear exchange restricts the allowed wavefunctions further. Nevertheless, "unambiguous evidence" for the Berry phase in the molecule Na_3 has been claimed (the citation is above.)