Phy 556 HW 6, answer to problem 2 – vibrations of a 2-d square molecule AB_4

The potential energy is $U=U_1 + U_2$, where

$$U_1 = \frac{1}{2}K_1\left[(x_1-x_0)^2+(y_2-y_0)^2+(x_3-x_0)^2+(y_4-y_0)^2\right]$$

$$U_2 = \frac{1}{4}K_2\left[(x_2-y_2-x_1+y_1)^2+(x_3+y_3-x_2-y_2)^2+(x_4-y_4-x_3+y_3)^2+(x_1+y_1-x_4-y_4)^2\right]$$

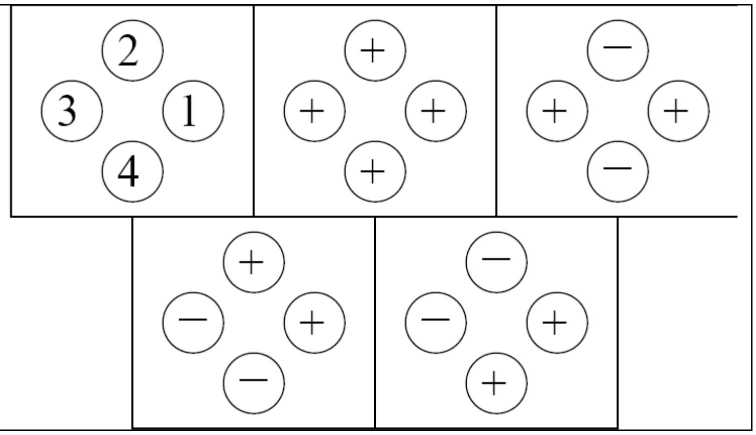
Newton's laws are expressed with mass-weighted coordinates as $\frac{d^2}{dt^2}|s\rangle = -\hat{D}|s\rangle$, where $\hat{D}=\hat{D}_1+\hat{D}_2$ and the 10-vector and 10 x 10 matrices are

$$|s\rangle = \begin{pmatrix} \sqrt{M}\,x_0 \\ \sqrt{M}\,y_0 \\ \sqrt{m}x_1 \\ \sqrt{m}y_1 \\ \sqrt{m}x_2 \\ \sqrt{m}y_2 \\ \sqrt{m}x_3 \\ \sqrt{m}y_3 \\ \sqrt{m}x_4 \\ \sqrt{m}y_4 \end{pmatrix} \quad \hat{D}_1 = \frac{K_1}{\sqrt{mM}}\begin{pmatrix} 2r & 0 & -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 2r & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 \\ -1 & 0 & 1/r & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 1/r & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 1/r & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/r \end{pmatrix} \text{with } r=\sqrt{\frac{m}{M}}$$

$$\text{and } \hat{D}_2 = \frac{K_2}{2m}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & -1 & 1 & 0 & 0 & -1 & -1 \\ 0 & 0 & 0 & 2 & 1 & -1 & 0 & 0 & -1 & -1 \\ 0 & 0 & -1 & 1 & 2 & 0 & -1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 2 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & -1 & 2 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & -1 & -1 & 0 & 2 & 1 & -1 \\ 0 & 0 & -1 & -1 & 0 & 0 & -1 & 1 & 2 & 0 \\ 0 & 0 & -1 & -1 & 0 & 0 & 1 & -1 & 0 & 2 \end{pmatrix}$$

The squared frequencies ω^2 are the eigenvalues of the full matrix $\hat{D}=\hat{D}_1+\hat{D}_2$. Group theory tells us some of the eigenvectors. The character table for the group C_{4v} is shown below to the left, and also, to the right, the numbering system for the four atoms of mass *m*. These atoms form a basis for the "permutation representation" which reduces to A_1+B_2+E. Basis functions for A_1 and B_2 are shown to the right in the top row, and for the E doublet, to the right in the bottom row. The specification B_2 (rather than B_1) derives from an (arbitrary) choice that σ_v planes pass through atoms and σ_d planes pass between them.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	+1	+1	+1	+1	+1
A_2	+1	+1	+1	-1	-1
B_1	+1	-1	+1	+1	-1
B_2	+1	-1	+1	-1	+1
E	+2	0	-2	0	0



The displacements of atoms ($|u\rangle$, like $|s\rangle$ except without the mass factor) are the basis for the 10-dimensional representation which transforms like the direct product of the 2-vector with the permutation representation (of all 5 atoms). A 2-vector transforms like E. The central atom does not mix with the others under rotations, and thus is an A_1 subspace. The displacements of the central atom thus transform as E. The other 8 degrees of freedom transform thus as E x (A_1 + B_2 + E). The representations E x A_1 and E x B_2 are both E representations, which consist of attaching x or y displacements to the atoms in the A_1 and B_2 patterns shown in the figure above. These E basis functions can be turned into normalized $|s\rangle$-vector basis functions most simply as follows

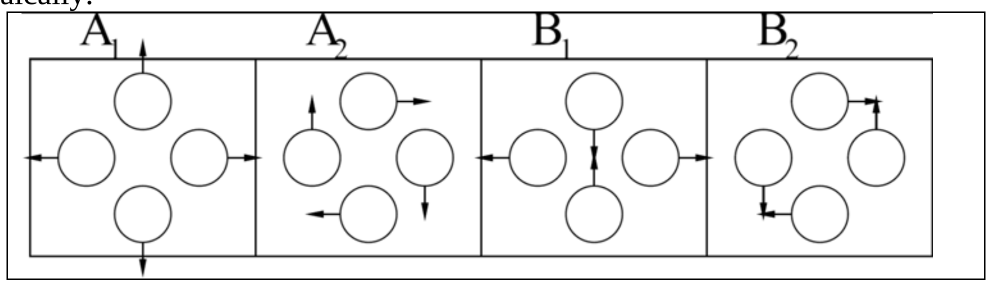
$$|x1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \; |x2\rangle = \frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \text{ and } |x3\rangle = \frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ -1 \\ 0 \end{pmatrix}$$ and similar for $|y1\rangle$, $|y2\rangle$, and $|y3\rangle$, except shifted down one entry to change x components into y components. The numbering 1,2,3 is arbitrary. If we take the 6 vectors just listed and compute $\langle\alpha|\hat{D}|\beta\rangle$, the resulting 6 x 6 matrix is guaranteed to block diagonalize into two identical 3 x 3 matrices, one for x components and one for y. But we can further simplify because we also are guaranteed that one eigenvector of each sub-block has eigenvalue 0 and corresponds to the uniform displacement in the x (or y) direction of the whole molecule. The uniform x-displacement is $|x0\rangle = \sqrt{M}|x1\rangle + 2\sqrt{m}|x2\rangle$. It is easy to verify that both $\hat{D}_1|x0\rangle$ and $\hat{D}_2|x0\rangle$ are zero. We then need to choose two basis functions orthogonal to $|x0\rangle$. The simplest choice is $|x\alpha\rangle = \left[2\sqrt{m}|x1\rangle - \sqrt{M}|x2\rangle\right]/\sqrt{M+4m}$ and $|x\beta\rangle = |x3\rangle$. Finally, we

compute the 2 x 2 matrices $\langle x\alpha|\hat{D}|x\beta\rangle$ (the y-version is of course identical.) The answer is

$$\left[\hat{D}_1\right]_{E'x} = \frac{K_1}{2m}\begin{pmatrix} \frac{M+4m}{M} & -\sqrt{\frac{M+4m}{M}} \\ -\sqrt{\frac{M+4m}{M}} & 1 \end{pmatrix} \text{ and } \left[\hat{D}_2\right]_{E'x} = \frac{2K_2}{m}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

Note that each of these two sub-systems has simple eigenvectors and one null eigenvalue. When the two spring constants K_1 and K_2 are both non-zero, the system is stable and the eigenvectors and eigenvalues are found by solving 2 x 2 matrices with no additional symmetry.

Finally, there are 4 more states belonging to E x E = $A_1 + A_2 + B_1 + B_2$, involving only the 4 outer masses m (the central mass M is stationary.) It is easy to "guess" the eigenvectors, and assign symmetry labels by the transformation properties listed in the character table. The eigenvectors are shown pictorially, and can thus be constructed algebraically.



$$|A_1\rangle = \frac{1}{2}\begin{pmatrix} 0\\0\\1\\0\\0\\1\\-1\\0\\0\\-1 \end{pmatrix},\ |A_2\rangle = \frac{1}{2}\begin{pmatrix} 0\\0\\0\\-1\\1\\0\\0\\1\\-1\\0 \end{pmatrix},\ |B_1\rangle = \frac{1}{2}\begin{pmatrix} 0\\0\\1\\0\\0\\-1\\-1\\0\\0\\1 \end{pmatrix},\ |B_2\rangle = \frac{1}{2}\begin{pmatrix} 0\\0\\0\\1\\1\\0\\0\\-1\\-1\\0 \end{pmatrix}$$

A_2 is a pure rotation with eigenvalue 0. A_1 is an eigenvector of $\hat{D}_1$ with eigenvalue K_1/m, and of $\hat{D}_2$ with eigenvalue $2K_2/m$, so the frequency is $\omega^2 = (K_1+2K_2)/m$. B_1 is an eigenvector of $\hat{D}_1$ with eigenvalue K_1/m, and of $\hat{D}_2$ with eigenvalue 0, so the frequency is $\omega^2 = K_1/m$. B_2 is an eigenvector of $\hat{D}_1$ with eigenvalue 0, and of $\hat{D}_2$ with eigenvalue $2K_2/m$, so the frequency is $\omega^2 = 2K_2/m$.