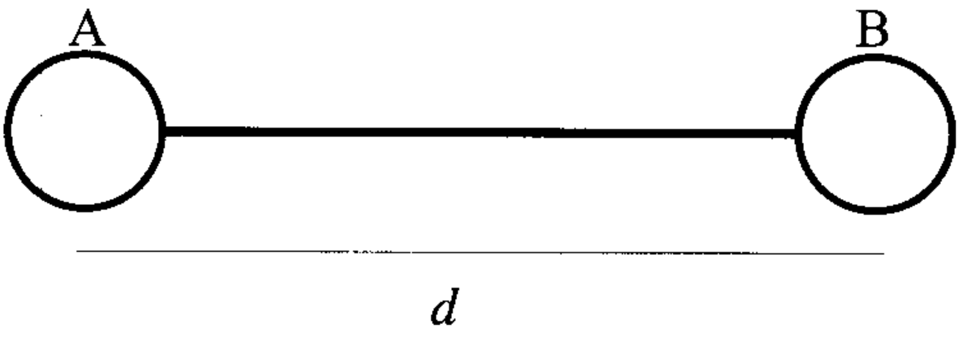
MSE 102, Fall 2009 Midterm #2

Write your name here: Solutions

Instructions:

- Answer all questions to the best of your abilities. Be sure to write legibly and state your answers clearly.
- The point values for each question are indicated.
- You are not allowed to use notes, friends, phones, etc.
- You can use calculators.
- There are a total of 100 points.
- Feel free to ask questions, but only for clarification purposes.



(1a) [15 POINTS] The figure above defines the structure of a molecule. Atoms A and B are the same type of atom, but are obviously sitting at different positions. Choosing the basis functions of the atom to be $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$, and assuming that these are both eigenfunctions of the bare atoms with energy eigenvalue $E_o = -1$, and that they are properly normalized and orthogonal to one another, construct the Hamiltonian matrix as we did in class. Assume that $-|\overline{V}| = -V_o/d$, with V_o a positive constant. Be sure to define the matrix elements explicitly. Use your Hamiltonian matrix to find the energies that one might measure for an electron in the dimer.

$$\underline{\underline{H}} = \begin{pmatrix} -1 & -V_o/d \\ -V_o/d & -1 \end{pmatrix}.$$

Here, $\int \psi_A^*(\underline{r})\, \hat{H}\, \psi_A(\underline{r})\, d\underline{r}$

$$\simeq \int \psi_A^*(\underline{r})\, \hat{H}_A \psi_A(\underline{r})\, d\underline{r} = E_o = -1$$

Similarly, $\int \psi_A^*(\underline{r})\, \frac{1}{2}(\hat{V}_A + \hat{V}_B)\, \psi_B(\underline{r})\, d\underline{r} \equiv -V_o/d$, and

$\int \psi_B^*(\underline{r})\, \hat{H}\, \psi_B(\underline{r})\, d\underline{r} = E_o = -1.$

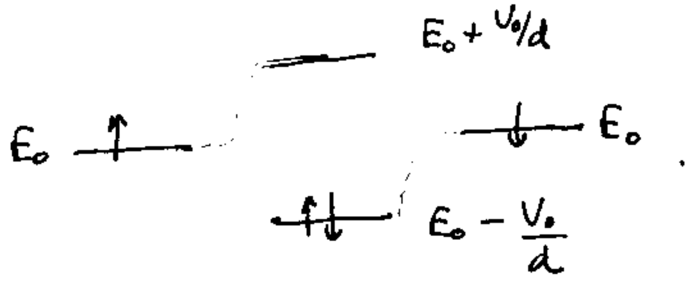
The energy eigenvalues satisfy $(-1-E)^2 - \frac{V_o^2}{d^2} = 0$

$\Rightarrow (E+1)^2 = \frac{V_o^2}{d^2}$ or $E = -1 \pm \frac{V_o}{d}.$

Hence an electron in the dimer may be found to have the energy $-1 - V_o/d$ or $-1 + \frac{V_o}{d}$.

(1b) [5 POINTS] Suppose that atoms A and B each have (initially) one electron bound to them. Compute the change in electronic energy associated with forming the dimer from two isolated atoms. Assume that the electrons do not interact with one another, or alternatively, that the electron-electron interaction is included in the definition of $\overline{V}$.

The energy level diagram looks something like this



The change in energy upon forming the bond is (electronic only)

$$\Delta E = E_f - E_i = 2\left(E_0 - \frac{V_0}{d}\right) - 2E_0 = -\frac{2V_0}{d}.$$

(1c) [5 POINTS] Now suppose that the binding part of the dimer energy is given solely by the change in electronic energy, and repulsive part of the energy is simply the repulsion between the two nuclei. Further suppose that this repulsive energy takes the form:

$$E_{rep}(d) = V_{rep}/d^2,$$

with V_{rep} a positive constant.

Compute the equilibrium bond length for the dimer and the total change in energy associated with forming the dimer from atoms that are initially separated by an infinite distance.

Total change in energy is

$$\Delta E_{total} = \frac{V_{rep}}{d^2} - 2\frac{V_0}{d}.$$

This energy is minimized when $\frac{\partial \Delta E_{total}}{\partial d} = 0.$

$$-\frac{2V_{rep}}{d^3} + \frac{2V_0}{d^2} = 0$$

$$\frac{V_{rep}}{d^3} = \frac{V_0}{d^2} \quad \text{or} \quad d = \frac{V_{rep}}{V_0} \Leftarrow \text{equilibrium bond length.}$$

$$\Delta E_{total}(\text{at Equilibrium}) = \frac{V_{rep}}{\left(\frac{V_{rep}}{V_0}\right)^2} - 2\frac{V_0}{V_{rep}/V_0}$$

$$= -\frac{V_0^2}{V_{rep}}.$$

(Note that this answer has the correct dimensions...)

(2a) [10 POINTS] Suppose that the interaction between two atoms is given by the Lennard-Jones potential:

$$V(d) = 4\varepsilon\left[\left(\frac{\sigma}{d}\right)^{12} - \left(\frac{\sigma}{d}\right)^{6}\right] \quad .$$

Choose $\varepsilon = 4.0$ eV, and $\sigma = 2.0$ Å. Consider a crystal with one atom per lattice vector and primitive lattice vectors:

$$\mathbf{a} = -a\,\mathbf{e}_y$$
$$\mathbf{b} = 2a\,\mathbf{e}_x$$

Find the equilibrium lattice parameter a for the crystal. Be sure to give the proper units. The following sums may be useful:

$\sum_{u=-\infty}^{\infty}\sum_{v=-\infty}^{\infty}\left(\frac{1}{u^2+4v^2}\right)^3 = 2.11107$ and $\sum_{u=-\infty}^{\infty}\sum_{v=-\infty}^{\infty}\left(\frac{1}{u^2+4v^2}\right)^6 = 2.00125$. (The sums exclude the singular terms.)

$$\frac{\text{Energy}}{\text{Atom}} = 2\varepsilon \sum_{uv}{}' \left[\left(\frac{\sigma}{|u\underset{\sim}{a}+v\underset{\sim}{b}|}\right)^{12} - \left(\frac{\sigma}{|u\underset{\sim}{a}+v\underset{\sim}{b}|}\right)^{6}\right].$$

Noting that $u\underset{\sim}{a}+v\underset{\sim}{b} = 2av\,\underset{\sim}{e}_x - ua\,\underset{\sim}{e}_y$, we find that $|u\underset{\sim}{a}+v\underset{\sim}{b}|^2 = 2^2v^2a^2 + u^2a^2$. Therefore, the energy per atom becomes:

$$\frac{E}{\text{atom}} = 2\varepsilon \sum_{u,v}{}' \left\{\left(\frac{\sigma}{a}\right)^{12}\left(\frac{1}{u^2+4v^2}\right)^{6} - \left(\frac{\sigma}{a}\right)^{6}\left(\frac{1}{u^2+4v^2}\right)^{3}\right\}$$

$$\equiv 2\varepsilon\left[A_{12}\left(\frac{\sigma}{a}\right)^{12} - A_6\left(\frac{\sigma}{a}\right)^{6}\right].$$

The true lattice parameter minimizes E/atom:

$$\frac{\partial(E/\text{atom})}{\partial a} = 2\varepsilon\left[\frac{-12A_{12}}{a}\left(\frac{\sigma}{a}\right)^{12} + \frac{6A_6}{a}\left(\frac{\sigma}{a}\right)^{6}\right] = 0$$

$$12\, A_{12}\left(\frac{\sigma}{a}\right)^6 = 6 A_6 \quad \text{or} \quad \left(\frac{\sigma}{a}\right)^6 = \frac{A_6}{2A_{12}} \quad \text{or} \quad a = \sigma\left(\frac{2A_{12}}{A_6}\right)^{1/6}.$$

Substituting, we find:

$$a = 2.0\,\text{Å} \times \left(\frac{2 \cdot 2.00125}{2.11107}\right)^{1/6} = 2.22502\,\text{Å}.$$

(2b) [5 POINTS] Evaluate the total energy per atom of the crystal at the equilibrium lattice parameter you calculated.

$$2\varepsilon\left[A_{12}\left(\frac{A_6}{2A_{12}}\right)^2 - A_6\left(\frac{A_6}{2A_{12}}\right)\right] = 2\varepsilon\left\{\frac{1}{4}\frac{A_6^2}{A_{12}} - \frac{1}{2}\frac{A_6^2}{A_{12}}\right\}$$

$$= -\frac{1}{2}\frac{A_6^2}{A_{12}}\varepsilon = -4.45383\ \frac{\text{eV}}{\text{atom}}.$$

(3) [10 POINTS] A cubic material is strained according to the following strain tensor:

$$\varepsilon = \begin{bmatrix} \alpha & 0 & \gamma \\ 0 & \alpha & 0 \\ \gamma & 0 & \alpha \end{bmatrix}.$$

Give the associated stress tensor in terms of the parameters α and γ and the elastic constants C_{11}, C_{12}, and C_{44}.

$\sigma_{ij} = C_{ijkl}\,\varepsilon_{kl}$. Substituting we have

$$\sigma_{11} = C_{11kl}\,\varepsilon_{kl} = C_{1111}\alpha + C_{1113}\gamma + C_{1122}\alpha + C_{1131}\gamma + C_{1133}\alpha$$

$$= C_{11}\alpha + C_{12}(\alpha + \alpha) = \alpha\,(C_{11} + 2C_{12})$$

$$\sigma_{12} = C_{12kl}\,\varepsilon_{kl} = 0$$

$$\sigma_{13} = C_{13kl}\,\varepsilon_{kl} = 2C_{44}\gamma$$

$$\sigma_{22} = C_{22kl}\,\varepsilon_{kl} = \alpha\,(2C_{12} + C_{11})$$

$$\sigma_{23} = C_{23kl}\,\varepsilon_{kl} = 0$$

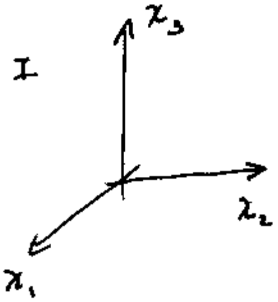
$$\sigma_{33} = \alpha\,(C_{11} + 2C_{12})$$

$$\therefore \quad \underset{\sim}{\sigma} = \begin{bmatrix} \alpha(C_{11} + 2C_{12}) & 0 & 2C_{44}\gamma \\ 0 & \alpha(C_{11} + 2C_{12}) & 0 \\ 2C_{44}\gamma & 0 & \alpha(C_{11} + 2C_{12}) \end{bmatrix}$$

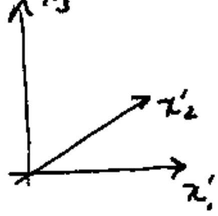
(4) [15 POINTS] A crystal has a four-fold axis of symmetry along its x_3-axis. What does this imply for a symmetric, second rank tensor property of the crystal? Support your answer with a *clear and detailed* mathematical argument.

If an object has a symmetry operation associated with it, application of that symmetry operation should leave the physical properties of the object unaltered. This particular object possesses a 4-fold axis. We have that the 2nd rank tensor should be identical in the frames sketched below:

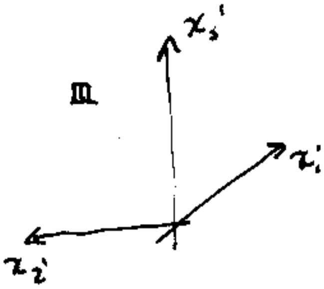
I



II

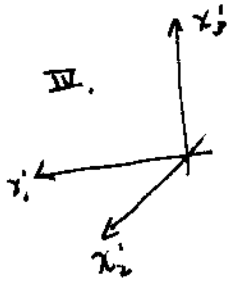


III



and

IV.



The matrix $\underline{\underline{a}}$ has components $a_{ij} = \underset{\sim}{e}_i' \cdot \underset{\sim}{e}_j$. Therefore

$$\underline{\underline{a}}^{II} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \underline{\underline{a}}^{III} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ ad } \underline{\underline{a}}^{IV} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The transformation rule for 2nd rank tensors reads:

$$\sigma_{ij}' = a_{ik} a_{jl} \sigma_{kl}.$$

We can apply this rule to derive constraints on the σ_{ij}'s.

Consider, first, the implications of transforming by $\underset{=}{a}^{II}$.

$$\sigma_{11}' = \sigma_{11} = a_{1k} a_{1l} \sigma_{kl} = (1)(1)\sigma_{22}. \qquad \therefore \ \sigma_{11} = \sigma_{22}$$

$$\sigma_{22}' = \sigma_{22} = a_{2k} a_{2l} \sigma_{kl} = (-1)(-1)\sigma_{11} \qquad \text{same conclusion.}$$

$$\sigma_{33}' = \sigma_{33} = a_{3k} a_{3l} \sigma_{kl} = (1)(1)\sigma_{33}$$

$$\sigma_{12}' = \sigma_{12} = a_{1k} a_{2l} \sigma_{kl} = (1)(-1)\sigma_{21}$$

this equation, coupled with the fact $\sigma_{12} = \sigma_{21}$ (symm. tensor) implies that $\sigma_{12} = 0$.

$$\left.\begin{aligned} \sigma_{23}' &= \sigma_{23} = a_{2k} a_{3l} \sigma_{kl} = (-1)(1)\,\sigma_{13} \\ \sigma_{13}' &= \sigma_{13} = a_{1k} a_{3l} \sigma_{kl} = (+1)(1)\,\sigma_{23} \end{aligned}\right\} \Rightarrow \begin{aligned} &\sigma_{23} = -\sigma_{13} = -\sigma_{23} \\ &\Rightarrow \ \sigma_{23} = \sigma_{13} = 0. \end{aligned}$$

Hence, as of now

$$\underset{\approx}{\sigma} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}.$$

Further application of the remaining symmetry operations yields no further reduction. Hence 2nd rank symmetric tensors for this crystal have the structure above.

(5a) [5 POINTS] An electron bound to a hydrogen atom is described by the wavefunction:

$$\Psi(\mathbf{r},t) = \frac{2i}{3}\exp\left(\frac{-iE_2 t}{\hbar}\right)\psi_{210}(\mathbf{r}) - \frac{\sqrt{5}}{3}\exp\left(\frac{-iE_3 t}{\hbar}\right)\psi_{32-1}(\mathbf{r}),$$

with $\psi_{nlm}(\mathbf{r})$ an eigenfunction of the Hamiltonian, $\hat{H}$, squared angular momentum, $\hat{L}^2$, and z-component of the angular momentum, $\hat{L}_z$.

Give the expectation value of the z-component of the angular momentum, $\hat{L}_z$, for the electron.

$$\langle \hat{L}_z \rangle = \left(\frac{2}{3}\right)^2 \hbar(0) + \frac{5}{9}\hbar(-1) = -\frac{5}{9}\hbar .$$

(5b) [5 POINTS] Give the expectation value of the total energy. (You can express this in terms of the energies E_2 and E_3.)

$$\langle \hat{H} \rangle = \frac{4}{9}E_2 + \frac{5}{9}E_3 .$$

(5c) [5 POINTS] Give the expectation value of the angular momentum squared, $\hat{L}^2$.

$$\langle \hat{L}^2 \rangle = \left(\frac{4}{9}\right)\hbar^2\, 1(1+1) + \frac{5}{9}\hbar^2\, 2(3)$$

$$= \hbar^2\left(\frac{8}{9} + \frac{30}{9}\right) = \frac{38}{9}\hbar^2$$

(6a) [5 POINTS] An electron bound to a one-dimensional nanowire is described by the wavefunction:

$$\Psi(x,t) = \frac{1}{3}\exp\left(\frac{-iE_2 t}{\hbar}\right)\psi_2(x) - \frac{1}{3}\exp\left(\frac{-iE_{42} t}{\hbar}\right)\psi_{42}(x) + \frac{\sqrt{7}}{3}\exp\left(\frac{-iE_7 t}{\hbar}\right)\psi_7(x),$$

with $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$ an eigenfunction of the Hamiltonian operator for the particle, and $E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$ the corresponding eigenvalue.

You conduct an experiment to measure the total energy of the particle. What values might you measure, and with what probability?

E_2 with probability $\frac{1}{9}$

E_{42} with probability $\frac{1}{9}$

E_7 with probability $7/9$.

(6b) [5 POINTS] At time t_1 you measure the energy to be E_{42}. Give an expression for the electron's wavefunction for all times greater than t_1.

$$\Psi(x,t) = e^{-iE_{42}(t-t_1)/\hbar}\,\psi_{42}(x).$$

(7) [10 POINTS] Suppose that the only point symmetry that a crystal possesses is the inversion operation. Prove that this implies that all odd rank tensors are identically zero, and that this symmetry operation places no constraints on the elements of even ranked tensors.

The transformation matrix associated with inversion is

$$\underline{\underline{a}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{or} \quad a_{ij} = -\delta_{ij}$$

Since inversion leaves the crystal invariant we have:

$$T'_{ij\ldots kl} = T_{ij\ldots kl} = a_{im}a_{jn}\cdots \cancel{a_{ok}a_{pl}}\, a_{ko}a_{lp}\, T_{mn\ldots op}$$

substituting

$$T_{ij\ldots kl} = (-\delta_{im})(-\delta_{jn})\cdots(-\delta_{ko})(-\delta_{lp})\, T_{mn\ldots op}\,.$$

performing the sums on the right

$$T_{ij\ldots kl} = (-1)^N\, T_{ij\ldots kl} \quad \text{with } N \text{ the rank of the}$$

tensor.

For N odd we have $T_{ij\ldots kl} = -T_{ij\ldots kl} = 0 \;\; \forall\, ij\ldots kl.$

For N even, this equation poses no constraints.