

## Set 3

**You must do problems I, IV, and V. You can choose to do either II and III (on molecules) or VI and VII on atoms. (You can't mix and match and, for example, do III and VII because that wouldn't be fair to anyone who did II and VI.)**

### I. Basis Sets, Secular Determinants, and the Mathematics of Computational Chemistry

We usually solve the Hartree-Fock equations,

$$\hat{f}(\mathbf{r})\psi_{\alpha}(\mathbf{r}) = \varepsilon_{\alpha}\psi_{\alpha}(\mathbf{r}), \quad (1.1)$$

by introducing what is called a basis set—a set of functions in terms of which we can expand the molecular orbitals. In terms of this basis set, we have

$$\psi_{\alpha}(\mathbf{r}) = \sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \quad (1.2)$$

and we then have

$$\hat{f}(\mathbf{r}) \left( \sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \right) = \varepsilon_{\alpha} \left( \sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \right) \quad (1.3)$$

Multiplying both sides by  $\chi_j(\mathbf{r})$  and integrating, we obtain

$$\sum_{i=1}^M \langle \chi_j | \hat{f} | \chi_i \rangle c_{i\alpha} = \varepsilon_{\alpha} \sum_{i=1}^M \langle \chi_j | \chi_i \rangle c_{i\alpha}. \quad (1.4)$$

If we define the Fock matrix,

$$f_{ij} \equiv \langle \chi_j | \hat{f} | \chi_i \rangle, \quad (1.5)$$

and the overlap matrix,

$$S_{ij} \equiv \langle \chi_j | \chi_i \rangle, \quad (1.6)$$

then Eq. (1.4) becomes what is called a generalized eigenvalue problem, namely

$$\mathbf{f}\mathbf{c}_{\alpha} = \varepsilon_{\alpha}\mathbf{S}\mathbf{c}_{\alpha} \quad (1.7)$$

where

$$\mathbf{c}_{\alpha} \equiv \begin{bmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{M\alpha} \end{bmatrix} \quad (1.8)$$

To solve the generalized eigenvalue problem, we write Eq. (1.7) as a homogeneous linear equation,

$$(\mathbf{f} - \varepsilon_{\alpha}\mathbf{S})\mathbf{c}_{\alpha} = \mathbf{0} \quad (1.9)$$

and note that this equation only has nontrivial solutions when the orbital eigenvalue,  $\varepsilon_{\alpha}$ , is chosen so that

$$|\mathbf{f} - \varepsilon_{\alpha}\mathbf{S}| = 0. \quad (1.10)$$

This is very similar to the “tricks” we used for diagonalizing a Hamiltonian matrix, except in this case the orbitals are not generally orthogonal, and so we cannot assume that  $\mathbf{S}$  is the identity matrix.

Often however, we have ignored the presence of  $S$ , and our decision to do so merits some justification. Consider a two-electron diatomic molecule, with orbital  $l$  being the 1s orbital for the “left-hand” atom and orbital  $r$  being the 1s orbital for the “right-hand” atom. In general, we have

$$\Psi(z_1, z_2) \equiv \frac{(\psi^{(l)}(\mathbf{r}_1) + \psi^{(r)}(\mathbf{r}_1))(\psi^{(l)}(\mathbf{r}_2) + \psi^{(r)}(\mathbf{r}_2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{2(1 + S)} \quad (1.11)$$

where the overlap integral is  $S = \langle \psi^{(l)} | \psi^{(r)} \rangle$ .

Now, consider what happens when we consider Löwdin's localized orbitals,

$$\begin{aligned} \phi^{(l)}(\mathbf{r}) &\equiv \frac{\left((1 + S)^{-1/2} + (1 - S)^{-1/2}\right)\psi^{(l)}(\mathbf{r}) + \left((1 + S)^{-1/2} - (1 - S)^{-1/2}\right)\psi^{(r)}(\mathbf{r})}{2} \\ \phi^{(r)}(\mathbf{r}) &\equiv \frac{\left((1 + S)^{-1/2} - (1 - S)^{-1/2}\right)\psi^{(l)}(\mathbf{r}) + \left((1 + S)^{-1/2} + (1 - S)^{-1/2}\right)\psi^{(r)}(\mathbf{r})}{2} \end{aligned} \quad (1.12)$$

**A. Show that  $\phi^{(l)}(\mathbf{r})$  and  $\phi^{(r)}(\mathbf{r})$  are orthogonal and normalized**

**B. Show that**

$$\Psi^L(z_1, z_2) \equiv \frac{(\phi^{(l)}(\mathbf{r}_1) + \phi^{(r)}(\mathbf{r}_1))(\phi^{(l)}(\mathbf{r}_2) + \phi^{(r)}(\mathbf{r}_2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{2} \quad (1.13)$$

is identical to Eq. (1.11).

**C. For the overlap of the 1s-orbitals between two atoms with atomic number  $Z$ , we have**

$$S = \left(1 + ZR + \frac{1}{3}Z^2R^2\right)e^{-ZR} \quad (1.14)$$

**For the Hydrogen molecule,  $R = 1.4011$ . Use Eq. (1.14) and plot either  $\phi^{(l)}(\mathbf{r})$  or  $\phi^{(r)}(\mathbf{r})$ . Compare to the 1s-orbitals.**

$$\begin{aligned} \psi_{1s}^{(l)}(\mathbf{r}) &\equiv \sqrt{\frac{Z^3}{\pi}} e^{-Z(\mathbf{r}-\mathbf{R}_l)} \\ \psi_{1s}^{(r)}(\mathbf{r}) &\equiv \sqrt{\frac{Z^3}{\pi}} e^{-Z(\mathbf{r}-\mathbf{R}_r)} \end{aligned} \quad (1.15)$$

We conclude that by choosing to interpret the atomic orbitals as localized atomic orbitals, we can replace the “generalized” eigenvalue problem in Eq. (1.9) with the “conventional” eigenvalue problem,

$$(\mathbf{f} - \varepsilon_\alpha \mathbf{I})\mathbf{c}_\alpha = \mathbf{0}. \quad (1.16)$$

As an example, we compare the  $\sigma$ -bonding structure in  $B_2$  and the  $F_2$  molecules and, in particular, the problem of  $sp$ -mixing. We have

$$\mathbf{f}_{B_2} \equiv \begin{matrix} \psi_{2s}^{(l)} \\ \psi_{2s}^{(r)} \\ \psi_{2p_z}^{(l)} \\ \psi_{2p_z}^{(r)} \\ \psi_{2p_x}^{(l)} \\ \psi_{2p_x}^{(r)} \\ \psi_{2p_y}^{(l)} \\ \psi_{2p_y}^{(r)} \end{matrix} \begin{bmatrix} -.56 & -.12 & 0 & .15 & 0 & 0 & 0 & 0 \\ -.12 & -.56 & -.15 & 0 & 0 & 0 & 0 & 0 \\ 0 & -.15 & -.31 & .1 & 0 & 0 & 0 & 0 \\ .15 & 0 & .1 & -.31 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.31 & -.05 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.05 & -.31 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.31 & -.05 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.05 & -.31 \end{bmatrix} \quad (1.17)$$

and

$$\mathbf{f}_{F_2} \equiv \begin{matrix} \psi_{2s}^{(l)} \\ \psi_{2s}^{(r)} \\ \psi_{2p_z}^{(l)} \\ \psi_{2p_z}^{(r)} \\ \psi_{2p_x}^{(l)} \\ \psi_{2p_x}^{(r)} \\ \psi_{2p_y}^{(l)} \\ \psi_{2p_y}^{(r)} \end{matrix} \begin{bmatrix} -1.47 & -.28 & 0 & .26 & 0 & 0 & 0 & 0 \\ -.28 & -1.47 & -.26 & 0 & 0 & 0 & 0 & 0 \\ 0 & -.26 & -.66 & .2 & 0 & 0 & 0 & 0 \\ .26 & 0 & .2 & -.66 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.66 & -.05 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.05 & -.66 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.66 & -.05 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.05 & -.66 \end{bmatrix} \quad (1.18)$$

A general principle is that when you can write a matrix in block diagonal form, then the eigenvalues and eigenvectors for each “block” can be found separately. For example, because there are no non-zero matrix elements between the  $\sigma$ -bonding orbitals  $\psi_{2s}(\mathbf{r})$  and  $\psi_{2p_z}(\mathbf{r})$  and the  $\pi$ -bonding orbitals,  $\psi_{2p_x}(\mathbf{r})$  and  $\psi_{2p_y}(\mathbf{r})$ , these orbitals do not mix. (This is clearly a consequence of orbital symmetry.) Similarly, the  $\pi_x$  and  $\pi_y$  orbitals do not mix, and since the  $2 \times 2$  matrices for these two problems are the same, the  $\pi_x$  and  $\pi_y$  orbitals are degenerate. Consequently, we can find the orbital energies for  $B_2$  by diagonalizing each of the following matrices:

- for the  $\sigma, \sigma^*$  orbitals

$$\mathbf{f}_{B_2}^{\sigma} \equiv \begin{matrix} \psi_{2s}^{(l)} \\ \psi_{2s}^{(r)} \\ \psi_{2p_z}^{(l)} \\ \psi_{2p_z}^{(r)} \end{matrix} \begin{bmatrix} -.56 & -.12 & 0 & .15 \\ -.12 & -.56 & -.15 & 0 \\ 0 & -.15 & -.31 & .1 \\ .15 & 0 & .1 & -.31 \end{bmatrix} \quad (1.19)$$

- for the  $\pi$ -orbitals,

$$\mathbf{f}_{B_2}^\pi \equiv \begin{pmatrix} \psi_{2p_x}^{(l)}, \psi_{2p_y}^{(l)} \\ \psi_{2p_x}^{(r)}, \psi_{2p_y}^{(r)} \end{pmatrix} \begin{bmatrix} -.31 & -.05 \\ -.05 & -.31 \end{bmatrix} \quad (1.20)$$

**D. Compute the orbital energies for the  $\pi$  and  $\sigma$  orbitals from Eq. (1.19) and (1.20). You will find it helpful to use a computer program to compute the eigenvalues in Eq. (1.19). (Mathcad, Mathematica, or Maple would suffice.)**

**E. Compute the orbital energies for  $F_2$  using Eq. (1.18). Notice the change in orbital ordering.**

It is often helpful to have a simple way to evaluate the eigenvalues of a 4x4 (or larger) matrix. Perturbation theory is particularly effective for this purpose. To do this, we can write

$$\begin{aligned} \mathbf{f}_{B_2}^\sigma &\equiv \mathbf{f}_{B_2}^{(0)} + \mathbf{f}_{B_2}' \\ &= \begin{bmatrix} -.56 & -.12 & 0 & 0 \\ -.12 & -.56 & 0 & 0 \\ 0 & 0 & -.31 & .1 \\ 0 & 0 & .1 & -.31 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & .15 \\ 0 & 0 & -.15 & 0 \\ 0 & -.15 & 0 & 0 \\ .15 & 0 & 0 & 0 \end{bmatrix} \end{aligned} \quad (1.21)$$

**F. Find the eigenvalues and eigenvectors of  $\mathbf{f}_{B_2}^{(0)}$ .**

Denoting the eigenvectors of  $\mathbf{f}_{B_2}^{(0)}$  as  $\{\mathbf{c}_\alpha\}_{\alpha=1}^4$  and the eigenvalues as  $\{\varepsilon_\alpha\}_{\alpha=1}^4$ , we find that the improved eigenvalues are

$$\mathbf{c}_\alpha^{pert.} \approx \mathbf{c}_\alpha + \sum_{\substack{i=1 \\ i \neq \alpha}}^4 \frac{(\mathbf{c}_i \cdot \mathbf{f}_{B_2}' \cdot \mathbf{c}_\alpha)}{\varepsilon_\alpha - \varepsilon_i} \mathbf{c}_i \quad (1.22)$$

The corrected eigenvalues are then

$$\varepsilon_\alpha^{pert.} \approx \varepsilon_\alpha + \sum_{\substack{i=1 \\ i \neq \alpha}}^4 \frac{(\mathbf{c}_\alpha \cdot \mathbf{f}_{B_2}' \cdot \mathbf{c}_i)(\mathbf{c}_i \cdot \mathbf{f}_{B_2}' \cdot \mathbf{c}_\alpha)}{\varepsilon_\alpha - \varepsilon_i} \quad (1.23)$$

**G. Calculate the correction to the  $\sigma_{2p_z}$  orbital energy using Eq. (1.23). Why is the only “non-vanishing” correction due to the  $\sigma_{2s}$  orbital? How does one interpret this shift in orbital energies?**

## II. Electronegativity, Hardness, and Electronegativity Equalization

The energy of an atom or molecule can be written in the form

$$E_0(N_0) \equiv \left\langle \Psi_0(N_0) \left| \sum_{i=1}^{N_0} \left[ -\frac{\nabla_i^2}{2} + v_0(\mathbf{r}_i) \right] + \sum_{j=i+1}^{N_0} \sum_{i=1}^{N_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \Psi_0(N_0) \right\rangle$$

Here, we have opted to explicitly denote the dependence of the energy, wave function, and Hamiltonian on the number of electrons,  $N_0$ . We can define

$$h(N_0) \equiv \left\langle \Psi_0(N_0) \left| -\frac{\nabla_1^2}{2} + v_0(\mathbf{r}_1) \right| \Psi_0(N_0) \right\rangle$$

$$v_{ee}(N_0) \equiv \left\langle \Psi_0(N_0) \left| \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \right| \Psi_0(N_0) \right\rangle$$

**A. Show that the energy can be written as**

$$E_0(N_0) = h(N_0) \cdot N_0 + v_{ee}(N_0) \cdot \frac{N_0(N_0-1)}{2}.$$

**B. In analogy to thermodynamics, the rate of change of the energy with respect to the number of electrons is called the electronic chemical potential,  $\mu(N_0)$ . Show that**

$$\mu(N_0) \equiv \left. \frac{\partial E_0(N)}{\partial N} \right|_{N_0}$$

$$= h(N_0) + \frac{N_0}{2} \left( 2 \cdot \left. \frac{\partial h(N)}{\partial N} \right|_{N_0} + \left( \frac{2N_0-1}{N_0} \right) v_{ee}(N_0) + (N_0-1) \left. \frac{\partial v_{ee}(N)}{\partial N} \right|_{N_0} \right) \quad (\text{II.1})$$

It is often an excellent approximation to assume that  $h(N_0)$  and  $v_{ee}(N_0)$  do not depend very strongly on the number of electrons. Thus,

$$\left. \frac{\partial h(N)}{\partial N} \right|_{N=N_0} \approx 0$$

$$\left. \frac{\partial v_{ee}(N)}{\partial N} \right|_{N=N_0} \approx 0 \quad (\text{II.2})$$

**C. The second derivative of the energy is related to the hardness of a molecular species,  $\eta(N_0)$ . Assuming that Eqs. (II.2) are exact, show that**

$$\eta(N_0) \equiv \left. \frac{\partial^2 E_0(N)}{\partial N^2} \right|_{N_0}$$

$$= v_{ee}(N_0) \quad (\text{II.3})$$

**D. Based on Eqs. (II.2) and the definition of the electronic chemical potential and the chemical hardness, derive the following expression for the energy as a function of the number of electrons,**

$$E(N) = E(N_0) + (N - N_0)\mu(N_0) + \frac{1}{2}(N - N_0)^2 \eta(N_0) \quad (\text{II.4})$$

Suppose we know, from experiment or calculation, the ionization potential,

$$I = E(N_0 - 1) - E(N_0),$$

and electron affinity,

$$A = E(N_0) - E(N_0 + 1)$$

of the system. We can use this information, plus Eqs. (II.1), (II.2), (II.3), and (II.4) to derive

$$v_{ee}(N_0) = \eta(N_0) = I - A \quad (II.5)$$

$$h(N_0) = -N_0(I - A) - A \quad (II.6)$$

$$\mu(N_0) = -\frac{I + A}{2} \quad (II.7)$$

$\frac{I+A}{2}$  is the Mulliken electronegativity of a molecule, so we infer from (II.7) that the electronic chemical potential is the negative of the electronegativity.

**E. Derive Eq. (II.5). (This is called Pariser's approximation; it is of great historical significance. Because evaluating electron-electron repulsion integrals is difficult, in the early days of quantum mechanics, people did not compute the electron-electron repulsion energy, but instead approximated it using experimental data.)**

Back in the 1950's R. T. Sanderson established the "electronegativity equalization principle," which states that when one performs an acid-base reaction, the base transfers electrons to the acid until the electronegativity of the two fragments equalize. It is not difficult to derive this result. Write the energy of the acid as

$$E_A(N_A) = E(N_A^0) + (N_A - N_A^0)\mu_A(N_A^0) + \frac{1}{2}(N_A - N_A^0)^2\eta_A(N_A^0) \quad (II.8)$$

where  $E_A(N_A)$  is the energy of the acid after charge transfer,  $N_A$  is the number of electrons on the acid after charge transfer,  $N_A^0$  is the number of electrons in the acid before charge transfer, and  $E_A(N_A^0)$ ,  $\mu_A(N_A^0)$ , and  $\eta_A(N_A^0)$  are the energy, chemical potential, and chemical hardness of the acid prior to charge transfer. Similarly, we write the energy of the base as

$$E_B(N_B) = E_B(N_B^0) + (N_B - N_B^0)\mu_B(N_B^0) + \frac{1}{2}(N_B - N_B^0)^2\eta_B(N_B^0) \quad (II.9)$$

The total number of electrons does not change during this reaction, so

$$N_A^0 + N_B^0 = N_A + N_B \quad (II.10)$$

and so the number of electrons transferred from the acid to the base must be given by.

$$\Delta N = N_A - N_A^0 = N_B^0 - N_B \quad (II.11)$$

Rewriting Eqs. (II.8) and (II.9) in obvious shorthand, we have that

$$\begin{aligned} E_A(N_A^0 + \Delta N) &= E_A^0 + \Delta N\mu_A + \frac{(\Delta N)^2}{2}\eta_A \\ E_B(N_B^0 - \Delta N) &= E_B^0 - \Delta N\mu_B + \frac{(\Delta N)^2}{2}\eta_B \end{aligned} \quad (II.12)$$

The energy of the product acid-base reaction,

$$A + B \rightarrow A - B \quad (II.13)$$

where  $\Delta N$  electrons are transferred from the acid to the base is then (approximately)

$$E_{AB}(\Delta N) = E_A(N_A^0 + \Delta N) + E_B(N_B^0 - \Delta N) \quad (II.14)$$

**F. Explain why finding the "ground state energy" of the product necessarily implies that the chemical potential of the acid and the base are equal.**

**G. Show that the optimum extent of charge transfer is given by**

$$\Delta N = \frac{\mu_B - \mu_A}{\eta_A + \eta_B} \quad (II.15)$$

The energy of the acid-base reaction, Eq. (II.13), can be written as

$$\Delta E_{AB}^{rxn}(\Delta N) = E_A(\Delta N) + E_B(\Delta N) - E_A - E_B \quad (\text{II.16})$$

**H. Show that the acid-base reaction is always exothermic, with (approximate) reaction energy**

$$\Delta E_{AB}^{rxn} = -\frac{(\mu_A - \mu_B)^2}{2(\eta_A + \eta_B)} \quad (\text{II.17})$$

**I. Show that the chemical potential of the acid *and* the base in the product is given by the same expression.**

(Hint: Use Eqs. (II.15), (II.8), and (II.9), along with the definition of the chemical potential.)

**J. Using the ionization potentials and electron affinities of the alkali metals and the halides, calculate the Mulliken electronegativity and hardness of these systems. (See the following table.) Estimate the charge on the halide in the associated species.**

Atom	Ionization Potential (eV)	Electron Affinity (eV)	Mulliken Electronegativity (eV)	Chemical Hardness (eV)
H	13.598	.754		
Li	5.392	.618		
Na	5.139	.548		
K	4.341	.501		
Rb	4.117	.486		
Cs	3.894	.472		
F	17.422	3.401		
Cl	12.967	3.613		
Br	11.814	3.364		
I	10.451	3.059		

### III. The Hard-Soft Acid-Base Principle

**You will find it helpful to do problem II before attempting this problem.**

You might question why, in problem II, we refer to

$$\eta(N_0) \equiv \left. \frac{\partial^2 E_0(N)}{\partial N^2} \right|_{N_0} = I - A \quad (\text{III.1})$$

as the chemical hardness. The definition was first proposed because of a strong correlation between  $I - A$  and the empirically observed hardnesses of atoms. This should be clear from part “M” of problem VIII. But does this definition of the hardness correspond to the Hard-Soft Acid-Base (HSAB) principle? The HSAB principle is, after all, the *raison d’être* for the concept of the hardness and indubitably the most important application of the concept.

In abstract terms, the HSAB principle says that: ***all other things being equal, hard acids prefer to bind to hard bases and soft acids prefer to bond to soft bases.*** In abstract terms, we write that the equilibrium in the “HSAB exchange reaction”



lies to the right. Here,  $A_h$  denotes the hard acid,  $B_h$  denotes the hard base,  $A_s$  denotes the soft acid, and  $B_s$  denotes the soft base. In the gas phase or in cases where the entropy and enthalpy of solvation are negligible, the fact that the equilibrium in Eq. (III.2) lies to the right is associated with the fact that the reaction is exothermic,  $\Delta U^{HSAB} < 0$ .

**A. Show that the internal energy change in reaction (III.2) can be written as**

$$\Delta U^{HSAB} = \frac{(\mu_{A_s} - \mu_{B_h})^2}{2(\eta_{A_s} + \eta_{B_h})} + \frac{(\mu_{A_h} - \mu_{B_s})^2}{2(\eta_{A_h} + \eta_{B_s})} - \frac{(\mu_{A_s} - \mu_{B_s})^2}{2(\eta_{A_s} + \eta_{B_s})} - \frac{(\mu_{A_h} - \mu_{B_h})^2}{2(\eta_{A_h} + \eta_{B_h})} < 0 \quad (\text{III.3})$$

(Hint: you will need to at least read (and preferably do) problem VIII in order to show this.)

Exceptions to the HSAB rule are common when the “all other things being equal” assumption is not accurate. In particular, the HSAB rule often fails when the strength (that is, the electronegativity) of the acids or bases involved in the reactions differ. Consequently, we require that the chemical potential of the hard and soft acids are the same. In addition, we require that the chemical potentials of the hard and soft bases are the same. Finally, since electrons will move from the bases to the acids, we require that the chemical potential of the base is greater than the chemical potential of the acid. We summarize these constraints by

$$\mu_A \equiv \mu_{A_h} = \mu_{A_s} < \mu_{B_h} = \mu_{B_s} \equiv \mu_B \quad (\text{III.4})$$

Now, let us suppose that the “hard” acid and “hard” base have hardnesses  $\xi$  times that of the “soft” acid and the “soft” base and that, moreover, the hard species both have the same hardness, while the soft species also both have the same hardness. That is, we assume that

$$\eta \equiv \eta_{A_s} = \eta_{B_s} \quad (\text{III.5})$$

$$\eta_{A_h} = \eta_{B_h} = \xi\eta \quad (\text{III.6})$$

**B. Using the assumptions in Eqs. (III.4)-(III.6), show that**

$$\Delta U^{HSAB} = -\frac{(\mu_A - \mu_B)^2 (\xi - 1)^2}{4\eta\xi(\xi + 1)} \quad (\text{III.7})$$

**Why is  $\Delta U^{HSAB}$  less than zero?**

## IV. The Long-Wavelength Approximation

Because the wavelength of light is much larger than the size of a molecule, we can assume that the molecule only sees an oscillating dipole field. We want to quantify this result further, and see where it might fail.

The most useful spectra for chemical purposes come from UV-vis spectroscopy (where one measures the energies of valence orbitals directly), but one can also obtain interesting information by from the X-ray regime, where one excites (or ionizes) core electrons. One can use this information to find the oxidation states of atoms, for instance and, by carefully monitoring absorbance and/or fluorescence, gain some information about the valence orbitals and orbital energies.

In the UV-regime, as discussed in class and in the notes, the wavelength of the radiation is generally much larger than the size of the orbitals with which it interacts, so the long-wavelength approximation works quite well. This is less clear in the X-ray regime, when we are considering, say, the ionization of the 1s orbital in Iron (or some other “heavy atom”). The energy of the 1s orbital is well approximated by the Hydrogenic formula,

$$E \approx -\frac{Z^2}{2} \quad (\text{IV.1})$$

and the orbital shape is quite close to



$$\psi(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \quad (\text{IV.2})$$

where  $Z$  is the atomic number in question. From problem I in problem set 3, we know that the average distance of an electron from the atom in a 1s orbital is given by

$$\begin{aligned} \langle r \rangle_{n,l,m} &\equiv \frac{1}{2Z} (3n^2 - l(l+1)) \\ &= \frac{3}{2Z} \end{aligned} \quad (\text{IV.3})$$

Combining what we know, then, we have that the ionization potential for a 1s-electron in an atom is approximate

$$IP \approx \frac{1}{2} Z^2 \quad (\text{IV.4})$$

and the size of the 1s-orbital is approximately.

$$R \approx \frac{3}{2Z} \quad (\text{IV.5})$$

Once the extent of an orbital is the same size as  $\frac{\lambda}{2}$ , then it is possible that one end of the molecule is in a strong negative field while the other end is in a strong positive field, and the long-wavelength approximation will not be valid. Indeed, the long-wavelength approximation will be questionable whenever the electric field changes more than a few percent over the extent of a molecule.

### A. A. At about what value of $Z$ does the long-wavelength approximate begin to break down for the excitation of the core electrons?

You may find it helpful that  $1 \text{ Hartree} = 4.359 \cdot 10^{-18} \text{ Joule}$ .

## V. Population Inversion and the Laser

This is a “classic” problem, wherein we relate what we have learned about spectroscopy to describe the populations of energy levels. This analysis actually dates all the way back to Einstein, who laid the groundwork for the discovery of the laser in 1917.

Let  $i$  denote the initial state of a system and  $f$  denote its final state; we assume the initial state has lower energy than the final state. Suppose the system is in equilibrium with an electromagnetic (=light) field, so that the number of molecules in the initial state,  $N_i$ , and the number of molecules in the final state,  $N_f$ . The rate at which molecules are excited from the initial state to the final state in the presence of light with energy density  $g(\hbar\omega)$  should be proportional to the energy density of the light and the number of molecules in the initial state. Einstein wrote the constant of proportionality as  $B_{fi}$ , and so the excitation rate is

$$\text{rate of absorbance} = B_{fi} \cdot g(\hbar\omega_{fi}) N_i \quad (\text{V.1})$$

We have noted that the rate of stimulated emission is the same as the rate of absorbance. Consequently, the rate of stimulate emission will be proportional to the energy density and the number of molecules in the final state, with the same constant of proportionality,  $B_{if} = B_{fi}$ . Thus

$$\text{rate of stimulated emission} = B_{fi} \cdot g(\hbar\omega_{fi}) N_f. \quad (\text{V.2})$$

As anyone who has ever done a spectrum knows, however, a molecule is quite capable of fluorescing even in the total absence of incident radiation. This process, known as spontaneous emission of light,<sup>1</sup> is

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<sup>1</sup> What exactly is spontaneous emission? It is a quantum effect, and if we had used a quantum theory for light the phenomenon of spontaneous emission would have fallen out of the theory very naturally. Essentially, every field has a “zeroth order” oscillation, and this is true even of the vacuum. The “vacuum oscillation” is associated with the creation and annihilation of a particle (or particles) in time, and can occur so long as the energy times the duration for which the particles exist is suitably small. More precisely, one has that  $\Delta E \Delta t \approx \frac{\hbar}{2}$ . So that a photon can “be created” provided it is “destroyed” again

clearly independent of the energy density in the incident light field and is proportional to the number of molecules in the excited state. Of course, the constant of proportionality is probably different from the proportionality constant for stimulated emission, since the two processes are fundamentally different. So we write the constant of proportionality as  $A_{fi}$  and have.

$$\text{rate of spontaneous emission} = A_{if}N_f \quad (\text{V.3})$$

$A_{fi}$  and  $B_{fi}$  are called the Einstein rate coefficients. Clearly, both coefficients are positive. There is, obviously, no such thing as “spontaneous absorption.”

### A. A. Derive a formula for $B_{fi}$ from Fermi's Golden Rule.

Using Eqs. (V.1)-(V.3), we can write the rate of change for the number of atoms in the initial

$$\frac{dN_i}{dt} = -B_{fi}g(\hbar\omega_{fi})N_i + B_{fi}g(\hbar\omega_{fi})N_f + A_{fi}N_f \quad (\text{V.4})$$

and “final” states,

$$\frac{dN_f}{dt} = +B_{fi}g(\hbar\omega_{fi})N_i - B_{fi}g(\hbar\omega_{fi})N_f - A_{fi}N_f \quad (\text{V.5})$$

### B. B. Comparing Eqs. (V.4) and (V.5), why is $N_i > N_f$ .

At equilibrium,  $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$ . We have, then, setting Eqs. (V.4) and (V.5) equal to one another, that

$$-B_{fi}g(\hbar\omega_{fi})N_i + B_{fi}g(\hbar\omega_{fi})N_f + A_{fi}N_f = B_{fi}g(\hbar\omega_{fi})N_i - B_{fi}g(\hbar\omega_{fi})N_f - A_{fi}N_f \quad (\text{V.6})$$

and so

$$\frac{N_f}{N_i} = \frac{B_{fi}g(\hbar\omega_{fi})}{B_{fi}g(\hbar\omega_{fi}) + A_{fi}} \quad (\text{V.7})$$

### C. C. Suppose the light source is very intense, so that $B_{fi}g(\hbar\omega_{fi})$ is much larger than $A_{fi}$ . Show that

$$\frac{N_f}{N_i} \approx 1 - \frac{A_{fi}}{B_{fi}g(\hbar\omega_{fi})} \quad (\text{V.8})$$

### D. D. Explain why, in a very intense light source, there is essentially no net absorbance of radiation. That is, why will light of frequency $\omega_{fi}$ shine “right through” a sample if it is strong enough.

We would like to find an expression for  $A_{fi}$ , but we don't want to have to do it the “right way” and consider the quantum theory of light. One way to do this is to put our system in an oven. Then, the relative populations of the final and initial states are given by the Boltzmann distribution, so

$$\frac{N_f}{N_i} = e^{-\hbar\omega_{fi}/kT} \quad (\text{V.9})$$

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The other unknown in Eq. (V.7),  $g(\hbar\omega_{fi})$ , is the intensity of the light source. However, the molecule is in an oven, so the light source is the black-body radiation from the oven's walls and, assuming these are also at temperature  $T$  (that is, our oven is perfectly insulated), we can use the black-body radiation law

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quickly enough. If the photon, however, stimulates a transition during its fleeting existence, after the “stimulating” photon has disappeared, the “stimulated” photon will still exist. Voila, “spontaneous” emission.

$$g(\hbar\omega_{fi}) = \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left( e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}. \quad (\text{V.10})$$

We substitute this results into Eq. (V.7) to obtain

$$\begin{aligned} e^{-\hbar\omega_{fi}/kT} &= \frac{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left( e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}}{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left( e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1} + A_{fi}} \\ e^{\hbar\omega_{fi}/kT} &= 1 + \frac{A_{fi}}{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left( e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}} \\ A_{fi} &= \frac{2\hbar\omega_{fi}^3}{\pi c^3} B_{fi}. \end{aligned} \quad (\text{V.11})$$

**E. The red-orange glow of hot hydrogen gas (remember the Hindenberg!) is due to the 3p-2s transition of the Hydrogen atom,  $A_{fi} = 6.7 \cdot 10^7 \frac{1}{s}$ . Compute  $\frac{N_f}{N_i}$  and  $\frac{A_{3p,2s}}{g(\hbar\omega)B_{3p,2s}}$  at  $T = 300^\circ K$ ,  $T = 10,000^\circ K$ , and  $T = 100,000^\circ K$ . What can you say about the relative rates of spontaneous emission,  $A_{fi}$  and stimulated emission,  $B_{fi}g(\hbar\omega_{fi})$  in the absence of light?**

How does a laser work? As a very simple case, we consider the “green line” for the Argon ion laser. This resembles a 3-level laser system, which is the simplest (but four-level lasers are more efficient) type of laser. The Argon ion is generated by a high-voltage electric discharge, which ionizes the Argon atom and excites it to a high-energy state, which then relaxes to the  $^4D_{5/2}$  state. This state then decays to the ground state  $^2P_{3/2}$ . However, because we have brought in a “third state” (the highly excited ion), we can achieve population inversion. This is helped by the fact that the excited state of interest decays very slowly (this is a spin-forbidden transition), so that  $A_{fi}$  is very small.

As an example that we can actually “solve”, we might consider a three-level system like the one shown below, which (vaguely) resembles the intensity-determining features of a four-level laser like the Nd-YAG laser. In this case, the system is “pumped” with light of frequency  $\omega_{31}$ , and then population inversion is achieved between the second and third states, causing a laser transition. We can write the rate coefficients as

$$\begin{aligned} \frac{dN_1}{dt} &= -g(\hbar\omega_{31})B_{31}N_1 + A_{21}N_2 + A_{31}N_3 + g(\hbar\omega_{31})B_{31}N_3 \\ \frac{dN_2}{dt} &= A_{32}N_3 - A_{21}N_2 \\ \frac{dN_3}{dt} &= g(\hbar\omega_{31})B_{31}N_1 - A_{32}N_3 - A_{31}N_3 - g(\hbar\omega_{31})B_{31}N_3 \end{aligned} \quad (\text{V.12})$$

and, as before, at equilibrium  $\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} = 0$ . From the second equation we find that

$$\frac{N_3}{N_2} = \frac{A_{21}}{A_{32}} \quad (\text{V.13})$$

Equation (V.13) is a general result, and can be easily understood (we probably could have guessed it). Clearly, we can have a laser only if  $N_3 > N_2$ , and it is best if  $N_3$  is much greater than  $N_2$  ( $N_3 \gg N_2$ ).

**F. F. From Eq. (V.13), what can you say about the relative spontaneous emission rates for the “higher” and “lower” energy states in a laser?**

**G. Based on Eq. (V.13), why do laser lines usually correspond to “forbidden transitions.”**

For example, if it were not for the perturbation inflicted on the  $\text{Nd}^{3+}$  ion by the  $\text{Y}_3\text{Al}_5\text{O}_{12}$  lattice, the popular Nd-YAG laser transition corresponding to  $A_{32}$  is electric dipole forbidden, magnetic dipole forbidden, electric quadrupole forbidden, and magnetic quadrupole forbidden, while the transition corresponding to  $A_{21}$  is electric dipole allowed.

## VI. Lifetime Broadening

Most of the effects that broaden spectral lines could be eliminated, in principle, by taking a spectrum at zero temperature and zero pressure and, in fact, high-resolution spectra are often taken under ultra-high vacuum conditions at liquid-helium temperatures. However, there is always a “homogeneous broadening” associated with spontaneous emission: there is no way to avoid the “decay time” associated with spontaneous emission, as it is an inherent property of the system.<sup>2</sup>

The rate of spontaneous decay is given by Eq. (V.3), and in order to relate this to expressions for homogeneous broadening (see the notes) we need to find the probability,  $P(\tau)$  that a molecule in its excited state at  $t = 0$  will still be in its excited state at  $t = \tau$ . The rate of transition is known from Eq. (V.3), and so the probability a molecule in its excited state at time  $t = \tau$  “emits” to the ground state (or, more properly, state  $i$ ), is proportional to the number of molecules in the excited state (which is proportional to  $P(\tau)$  if the light source measuring the absorption spectrum is not very powerful), so we have

$$dP(\tau) = -A_{fi}P(\tau)d\tau. \quad (\text{VI.1})$$

**A. A. Show that  $P(\tau) = e^{-A_{21}\tau}$ .**

The natural lifetime of an excited state is defined as the time it takes for  $P(\tau)$  to decay from  $P(0) = 1$  to  $P(\tau) = \frac{1}{e}$  in the absence of external fields. It follows from the definition and Eq. (VI.1) that the lifetime of a state is

$$\tau \equiv \frac{1}{A_{21}}. \quad (\text{VI.2})$$

**B. B. Referring to the section on homogeneous broadening in the notes, show that the line shape is given by**

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{8\pi} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 \left[ \frac{(A_{21})}{A_{21}^2 + (\omega - \omega_{fi})^2} - \frac{(A_{21})}{A_{21}^2 + (\omega + \omega_{fi})^2} \right]. \quad (\text{VI.3})$$

If we assume that the initial state is the ground state ( $i = 0$ ), that the incident light is very weak (so  $p_0 \approx 1$  and  $p_f \approx 0$ ), we find that

$$I(\omega) \equiv \frac{1}{8\pi} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 \left[ \frac{(A_{f0})}{A_{f0}^2 + (\omega - \omega_{fi})^2} - \frac{(A_{f0})}{A_{f0}^2 + (\omega + \omega_{fi})^2} \right]. \quad (\text{VI.4})$$

<sup>2</sup> This is a lie. There is a weird quantum-mechanical result that says that if you constantly observe a system it can never change its state. For obvious reasons, it is called the “watched pot paradox.” But “constantly observing” a system is extremely difficult and is not done in the context of chemical spectroscopy.

**C. C. Plot Eq. (VI.4), assuming that the “pre-factor” is equal to  $\frac{1}{\pi}$ .**

**D. The full-width at half-maximum of the spectral line you just plotted is**

$$2A_{21} = \frac{2}{\tau} \quad (\text{VI.5})$$

Putting the molecule in any external field at all with broaden the line further and shorten the lifetime of the excited state. The error in frequency of the excited state, then, is always greater than

$$\Delta\omega \geq 2A_{21} = \frac{2}{\tau} \quad (\text{VI.6})$$

and so the energy uncertainty in the spectral line satisfies the inequality

$$\Delta E \equiv \hbar\Delta\omega \geq \hbar\frac{2}{\tau} \quad (\text{VI.7})$$

$$\tau\Delta E \geq \frac{\hbar}{2}$$

Equation (VI.7) is sometimes called the “energy-time” uncertainty principle but it should be clear that it is really just a manifestation of the fundamental relationship from the Fourier transform, which is usually stated

$$\Delta t \cdot \Delta\nu \geq \frac{1}{2}. \quad (\text{VI.8})$$

One of the most important uses of spectral states with long lifetimes is the laser, as discussed in the previous problem. Another important use is in the measurement of time. The *definition* of a second is that the time it takes for 9192631770 periods of the oscillation associated with the hyperfine splitting in the  $^{133}\text{Cs}$  atom. (This is the basis of the “atomic clocks” used in satellite positioning systems.)

Clearly, in order to define a “second” in this way we must know the frequency of an oscillation very accurately, and this can only be done if width of the spectral line corresponding to a transition is very, very small.

The longest lived electronic excited state we know of is the  $^2F_{7/2}$  to  $^2S_{1/2}$  transition for  $^{172}\text{Yb}^+$ , which has a characteristic wavelength of 467 nm and a lifetime of about 8.4 years. (The transition is electric *octupole* allowed.) According to Eq. (VI.8), we should be able to measure the frequency of the transition with an error of only about

$$\Delta\nu \approx \frac{1}{2\tau} \quad (\text{VI.9})$$

and, in practice, we can do slightly better than this.

**E. D. Approximate the inherent uncertainty in the frequency of the  $^2F_{7/2}$  to  $^2S_{1/2}$  transition. What is the relative error in the frequency of the transition?**

**F. E. What is the inherent error in the period of this oscillation? How many oscillations are there (roughly) per second? What is the theoretical limit on the accuracy with which the number of oscillations per second can be measured?**

**G. F. What is the approximate error in the wave length? What is the relative error in the wavelength?**

(You can compute this by computing the wavelength for  $\nu + \Delta\nu$  and  $\nu$ , and comparing.)

We can compare this transition to a (typical) transition in  $^{172}\text{Yb}^+$ . For example, the  $^2P_{1/2}$  to  $^2S_{1/2}$  transition has a wavelength of 369 nm and a lifetime of 8 ns.

**H. Approximate the inherent uncertainty in the frequency of the  $^2P_{1/2}$  to  $^2S_{1/2}$  transition.**

**I. H. What is the approximate absolute error in the wave length?**

Note that states with long lifetimes have “very pure” frequencies and wavelengths—they give very monochromatic light. This is yet another reason why, in designing lasers, one tends to prefer states with long lifetimes as the “initial state” for stimulated emission.

## VII. Selection Rules

When deriving selection rules, one's life is made much easier if one remembers that given any odd function of  $x$ ,<sup>3</sup> then

$$\int_{-a}^a f(x) dx = 0 \quad (\text{VII.1})$$

- A. A. Derive Eq. (VII.1) from the definition of an odd function.**
- B. B. For the one-electron atom, use Eq. (VII.1) to explain why**
  - (a) transitions from one s-orbital to another s-orbital are dipole forbidden.**
  - (b) transitions from one p-orbital to another p-orbital are dipole forbidden.**
  - (c) transitions from an s-orbital to a d-orbital are dipole forbidden.**
  - (d) transitions from the 1s to the 2p orbital are dipole allowed**

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<sup>3</sup> A function is odd if  $f(x) = -f(-x)$ . A function is even if  $f(x) = f(-x)$ .