Final Examination

Chemistry 3BB3; Winter 2004

101 points are available on the test.

Part 1. Closed-Book Derivations/Problems (Each piece of each problem is worth 2 points. 46 points total)

1. Derive the Born-Oppenheimer Approximation:

(a) Write the full Schrödinger equation, for both the nuclei and the electrons, for a molecule with n nuclei and m electrons. ***Do not use atomic units.*** (n and m should be used in your formula!)

$$\left(\begin{aligned} &\sum_{\alpha=1}^{n} -\frac{\hbar^2 \nabla_\alpha^2}{2M_\alpha} + \sum_{i=1}^{m} -\frac{\hbar^2 \nabla_i^2}{2m_e} - \sum_{i=1}^{m}\sum_{\alpha=1}^{n} \frac{Z_\alpha e^2}{4\pi\varepsilon_0 \left| r_i - R_\alpha \right|} \\ &+ \sum_{i=1}^{m}\sum_{j=i+1}^{m} \frac{e^2}{4\pi\varepsilon_0 \left| r_i - r_j \right|} + \sum_{\alpha=1}^{n}\sum_{\beta=\alpha+1}^{n} -\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 \left| R_\alpha - R_\beta \right|} \end{aligned} \right) \Psi\left(r_1, \ldots r_m; R_1, \ldots R_n \right) = E\Psi\left(r_1, \ldots r_m; R_1, \ldots R_n \right)$$

(b) Using atomic units, what is the full Schrödinger equation for the Hydrogen molecule?

$$\left(\sum_{\alpha=1}^{2} -\frac{\nabla_\alpha^2}{2m_p} + \sum_{i=1}^{2} -\frac{\nabla_i^2}{2} - \sum_{i=1}^{m}\sum_{\alpha=1}^{n} \frac{1}{\left| r_i - R_\alpha \right|} + \frac{1}{\left| r_1 - r_2 \right|} + \frac{1}{\left| R_1 - R_2 \right|} \right) \Psi\left(r_1, r_2; R_1, R_2 \right) = E\Psi\left(r_1, r_2; R_1, R_2 \right)$$

m_p is the proton mass measured in units of m_e.

(c,d) For the Hydrogen molecule, H_2, derive the electronic and nuclear Schrödinger equations in the Born-Oppenheimer approximation. Indicate each approximation you make. Discuss its validity in a sentence or so.

The key idea is separation of variables, wherein the position of the electrons is considered to be dependent of the position of the nuclei, but not their motion. To this end, we write the wave function as the product of an electronic and nuclear component:

$$\Psi_{k\nu}\left(r_1, r_2, R_A, R_B \right) = \psi_k\left(r_1, r_2; R_A, R_B \right) \chi_{k\nu}\left(R_A, R_B \right)$$

We substitute into part (b) and use the identity

$$\nabla_A^2 \psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right) = \chi\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_A^2\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right) + \psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_A^2\chi\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$+2\nabla_A\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\cdot\nabla_A\chi\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

to obtain

$$\left[-\frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

$$\left(-\frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p}\right)\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$+\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

$$\left(\frac{-1}{2m_p}\right)\left[\begin{array}{l}\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_A^2\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right) + \psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_A^2\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right) \\ +2\nabla_A\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\cdot\nabla_A\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right) + \chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_B^2\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right) \\ +\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\nabla_B^2\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right) + 2\nabla_B\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\cdot\nabla_B\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\end{array}\right]$$
$$+\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

$$\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p} - \frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$\textcolor{blue}{-\frac{\nabla_A\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\cdot\nabla_A\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)}{m_p} - \frac{\nabla_B\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\cdot\nabla_B\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)}{m_p}} + \chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p} - \frac{-\nabla_A^2}{2m_p}\right)\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$+\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

We note that because the mass of the proton is much larger (almost 2000 times larger!) than the mass of the electron, the blue terms are quite small compared to those that come afterwards. We set the blue terms equal to zero, which amounts to assuming that because the nuclei move much more slowly than the electrons, the nuclei can be considered "fixed" on the time scale of electronic motion. Neglecting these terms, we obtain

$$\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p} - \frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$+\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)$$
$$= E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}_A, \boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A, \boldsymbol{R}_B\right)$$

which is the classic form of the Schrödinger equation from separation of variables. We then solve the electronic Schrödinger equation

$$\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2}-\frac{1}{|r_i-\boldsymbol{R}_A|}\right)+\frac{1}{|r_1-r_2|}+\frac{1}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}\right]\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)\equiv U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)\ (\text{C-1-A})$$

and substitute this result into the previous result, obtaining the nuclear Schrödinger equation

$$\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)+\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$
$$=E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$
$$\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}+U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)=E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_A,\boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$
$$\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}+U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)=E_{k\nu}^{BO}\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$

which gives the interpretation of the nuclei moving on the potential energy surface, $U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)$ due to the electrons in the system.

2. Hydrogenic Wave Functions.

(a) Show that

$$\psi(\boldsymbol{r}) \propto \left(6Zr - Z^2 r^2\right) e^{-Zr/3} Y_1^1(\theta, \phi)$$

is an eigenfunction of the of the Hydrogenic atom.

The Schrödinger equation for the Hydrogenic atom, in spherical coordinates, is:

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat{L}^2(\theta,\phi)}{r^2}\right] - \frac{Z}{r}\right)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Substituting, we have

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat{L}^2(\theta,\phi)}{r^2}\right] - \frac{Z}{r}\right)\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi)$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right] - \frac{Z}{r}\right)\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi) + \frac{\hat{L}^2(\theta,\phi)}{2r^2}\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi)$$

$$Y_1^1(\theta,\phi)\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right] - \frac{Z}{r}\right)\left(6Zr - Z^2r^2\right)e^{-Zr/3} + \left(6Zr - Z^2r^2\right)e^{-Zr/3}\frac{2Y_1^1(\theta,\phi)}{2r^2} = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}Y_1^1(\theta,\phi)$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right] - \frac{Z}{r} + \frac{1}{r^2}\right)\left(6Zr - Z^2r^2\right)e^{-Zr/3} = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right]\left(6Zr - Z^2r^2\right)e^{-Zr/3} - \left[\left(6Z^2 - Z^3r\right) - \frac{6Z}{r} + Z^2\right]e^{-Zr/3}\right) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\right]\left[\left(6Z - 2Z^2r\right)e^{-Zr/3} - \frac{Z}{3}\left(6Zr - Z^2r^2\right)e^{-Zr/3}\right] - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right)e^{-Zr/3}\right) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\right]\left[6Zr^2 - 2Z^2r^3 - 2Z^2r^3 + \frac{Z^3}{3}r^4\right]e^{-Zr/3} - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right)e^{-Zr/3}\right) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\right]\left[6Zr^2 - 4Z^2r^3 + \frac{Z^3}{3}r^4\right]e^{-Zr/3} - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right)e^{-Zr/3}\right) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left(\frac{1}{r^2}\right)\left[\left[12Zr - 12Z^2r^2 + \frac{4Z^3}{3}r^3\right]e^{-Zr/3} + \frac{-Ze^{-Zr/3}}{3}\left[6Zr^2 - 4Z^2r^3 + \frac{Z^3}{3}r^4\right]\right] - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right)e^{-Zr/3}\right) = E\left(6Zr - Z^2r^2\right)e^{-Zr/3}$$

$$\left(-\frac{1}{2}\left(\frac{1}{r^2}\right)\left[\left[12Zr - 12Z^2r^2 + \frac{4Z^3}{3}r^3\right] + \frac{-Z}{3}\left[6Zr^2 - 4Z^2r^3 + \frac{Z^3}{3}r^4\right]\right] - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right)\right) = E\left(6Zr - Z^2r^2\right)$$

$$-\frac{6Z}{r} + 6Z^2 - \frac{2Z^3}{3}r + Z^2 - \frac{2Z^3}{3}r + \frac{Z^4r^2}{18} - \left(7Z^2 - Z^3r - \frac{6Z}{r}\right) = E\left(6Zr - Z^2r^2\right)$$

$$\frac{-4Z^3}{3}r + Z^3r + \frac{Z^4r^2}{18} = E\left(6Zr - Z^2r^2\right)$$

$$\frac{Z^2}{18}\left(-24Zr + 18Zr + Z^2r^2\right) = E\left(6Zr - Z^2r^2\right)$$

$$\frac{-Z^2}{18} = E$$

So this is the 3p wavefunction for the hydrogenic atom.

(b) What is the energy of this state in <u>SI</u> units?

$$E = -\frac{Z^2 m_e e^4}{\left(4\pi\varepsilon_0\right)^2 18\hbar^2}$$

3.   Integral Hellmann-Feynman Theorems

(a)   Derive the Integral Hellmann-Feynman Theorem:

$$E(\lambda_2) - E(\lambda_1) = \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}$$

We have that

$$\frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} = \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}$$

$$= \frac{\langle \hat{H}(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}.$$

In the second line we use the fact that the Hamiltonian is a Hermitian operator. Using the fact that $\Psi(\lambda_{1,2})$ is an eigenfunction of $\hat{H}(\lambda_{1,2})$ with eigenvalue $E(\lambda_{1,2})$, we have that

$$\frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} = \frac{\langle \hat{H}(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}$$

$$= \frac{\langle E(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | E(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}$$

$$= E(\lambda_2) \frac{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - E(\lambda_1) \frac{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}$$

$$= E(\lambda_2) - E(\lambda_1)$$

which completes the proof.

4.   Term Symbols:

(a)   List the term symbols for a [closed shell] $5d^2\, 4f^1$ **electron configuration.**

The microstates for the $5d^2$ configuration are obtained from

M_S/M_L	4	3	2	1	0

1	0	$\left|\psi_{5d_2}\alpha\ \psi_{5d_1}\alpha\right|$ $\left|\psi_{5d_2}\alpha\ \psi_{5d_0}\alpha\right|$	$\left(\begin{array}{c}\left|\psi_{5d_1}\alpha\ \psi_{5d_0}\alpha\right|\\\left|\psi_{5d_2}\alpha\ \psi_{5d_{-1}}\alpha\right|\end{array}\right)$	$\left(\begin{array}{c}\left|\psi_{5d_1}\alpha\ \psi_{5d_{-1}}\alpha\right|\\\left|\psi_{5d_2}\alpha\ \psi_{5d_{-2}}\alpha\right|\end{array}\right)$

$$M_S/M_L\quad 4\qquad\qquad 3\qquad\qquad\quad 2\qquad\qquad\quad 1\qquad\qquad\quad 0$$

$$1\qquad 0$$

$$0\qquad \left|\psi_{5d_2}\alpha\ \psi_{5d_2}\beta\right|$$

This gives us the terms $^3F, {}^3P, {}^1G, {}^1D, {}^1S$.

Coupling these terms with the $4f$ electron, we have

$$^3F \rightarrow {}^4I, {}^4H, {}^4G, {}^4F, {}^4D, {}^4P, {}^4S$$
$$\rightarrow {}^2I, {}^2H, {}^2G, {}^2F, {}^2D, {}^2P, {}^2S$$
$$^3P \rightarrow {}^4G, {}^4F, {}^4D, {}^4P, {}^4S$$
$$\rightarrow {}^2G, {}^2F, {}^2D, {}^2P, {}^2S$$
$$^1G \rightarrow {}^2J, {}^2I, {}^2H, {}^2G, {}^2F, {}^2D, {}^2P$$
$$^1D \rightarrow {}^2H, {}^2G, {}^2F, {}^2D, {}^2P, {}^2S$$
$$^1S \rightarrow {}^2F, {}^2D, {}^2P, {}^2S$$

(b)   What is the ground state term according to Hund's rules? What are the possible values of J for this term?

Ground state is ^4I .

$$J = |L+S|, |L+S-1|, \dots |L-S| = \left|6+\tfrac{3}{2}\right|, \left|6+\tfrac{3}{2}-1\right|, \dots \left|6-\tfrac{3}{2}\right| = \tfrac{15}{2}, \tfrac{13}{2}, \tfrac{11}{2}, \tfrac{9}{2}$$

5.   The Non-Crossing Rule

(a,b) Derive the non-crossing rule. That is, describe why, for a two states of a diatomic molecule, described with wave functions $\Psi_1(R, \tau)$ and $\Psi_2(R, \tau)$, will (i) never cross if Ψ_1 and Ψ_2 have the same symmetry, but (ii) may cross if Ψ_1 and Ψ_2 have different symmetry. Here τ denotes all the electronic coordinates of the molecule, and R is the bond length of the diatomic. You can treat the more general case of a polyatomic molecule if you wish to, but you do not have to.

Let $\Psi_1(R)$ and $\Psi_2(R)$ denote two approximate eigenstates for a given value bond length, R.   We can improve the approximation by mixing the two states; obtaining new states that are a linear combination of the old states.

$$\Psi_1^{better}(R) = a\Psi_1(R) + \sqrt{1 - |a|^2}\,\Psi_2(R)$$
$$\Psi_2^{better}(R) = \sqrt{1 - |a|^2}\,\Psi_1(R) - a\Psi_2(R)$$

To find a we, solve the eigenvalue problem

$$\begin{bmatrix} \left\langle \Psi_1(R)\left|\hat{H}\right|\Psi_1(R)\right\rangle & \left\langle \Psi_1(R)\left|\hat{H}\right|\Psi_2(R)\right\rangle \\ \left\langle \Psi_2(R)\left|\hat{H}\right|\Psi_1(R)\right\rangle & \left\langle \Psi_2(R)\left|\hat{H}\right|\Psi_2(R)\right\rangle \end{bmatrix}\begin{bmatrix} a_k \\ b_k \end{bmatrix} = E_k \begin{bmatrix} a_k \\ b_k \end{bmatrix}$$

$$\begin{bmatrix} E_1(R) & \left\langle \Psi_1(R)\left|\hat{H}\right|\Psi_2(R)\right\rangle \\ \left\langle \Psi_2(R)\left|\hat{H}\right|\Psi_1(R)\right\rangle & E_2(R) \end{bmatrix}\begin{bmatrix} a_k \\ b_k \end{bmatrix} = E_k \begin{bmatrix} a_k \\ b_k \end{bmatrix}$$

The solutions to this eigenvalue problem are found by solving

$$\begin{vmatrix} E_1(R) - E_k^{better} & \left\langle \Psi_1(R)\left|\hat{H}\right|\Psi_2(R)\right\rangle \\ \left\langle \Psi_2(R)\left|\hat{H}\right|\Psi_1(R)\right\rangle & E_2(R) - E_k^{better} \end{vmatrix} = 0$$

This gives a quadratic equation, with solutions

$$E_{1,2}^{better}(R) = \frac{E_1(R) + E_2(R)}{2}$$
$$\pm \frac{\sqrt{\left(E_1(R) - E_2(R)\right)^2 - 4\left|\left\langle \Psi_1(\{\boldsymbol{R}_\alpha\})\left|\hat{H}\right|\Psi_2(\{\boldsymbol{R}_\alpha\})\right\rangle\right|^2}}{2}$$

If the two potential energy surfaces did cross then the discriminant (the term in the square root) must be zero. This implies that both

$$E_1(R) = E_2(R)$$

and

$$\left\langle \Psi_1(R) \middle| \hat{H} \middle| \Psi_2(R) \right\rangle = 0 \,.$$

This gives two nonlinear equations but there is only one unknown, R. There will not be a solution, in general. However, when Ψ_1 and Ψ_2 have different symmetry, $\left\langle \Psi_1(R) \middle| \hat{H} \middle| \Psi_2(R) \right\rangle = 0$ holds automatically. In that case, we have one equation and one unknown, and so the curves can cross for certain values of R.

(c) **What does the non-crossing rule have to do with the construction of the correlation diagram we used to connect the "united-atom" and "separated atom" limits of a diatomic molecule?**

The non-crossing rule gives us the rules for connecting united-atom and separated-atom states. In particular, because curves with the same symmetry cannot cross, the kth-lowest energy state of a given symmetry in the united-atom limit must correspond to the kth-lowest energy state of the same symmetry in the separated atom limit. Were this not to be the case—where the kth lowest state of one symmetry to be connected with the lth lowest state of the same symmetry (with $l \neq k$), then curves of the same symmetry would cross, which is forbidden.

6. Time-Dependence of the Wave function.

(a) **Using the time-dependent Schrödinger equation, derive the formula for the time-dependent wave function of a stationary state, $\Psi_k\left(r_1,\dots,r_N;R_1,\dots,R_P;t\right)$, in terms of the solution to the time-independent Schrödinger equation,**

$$\hat{H}_{molecule}\Phi_k\left(r_1,\dots,r_N;R_1,\dots,R_P\right) = E_k\Phi_k\left(r_1,\dots,r_N;R_1,\dots,R_P\right)$$

Using separation of variables, write

$$\Psi_k\left(r_1,\dots,r_N;R_1,\dots,R_P;t\right) = \Phi_k\left(r_1,\dots,r_N;R_1,\dots,R_P\right)\chi_k\left(t\right)$$

Then, substituting into the time-dependent Schrödinger equation we have

$$\hat{H}_{molecule}\Psi_i = i\hbar\frac{\partial\Psi_i}{\partial t}$$

$$E_i\Phi_i\chi_i = i\hbar\frac{\partial\Phi_i\chi_i}{\partial t}$$

$$E_i\Phi_i\chi_i = i\hbar\Phi_i\frac{\partial\chi_i}{\partial t}$$

$$\frac{1}{i\hbar}E_i\,dt = \frac{1}{\chi_i}\,d\chi_i$$

$$\frac{-i}{\hbar}\int E_i\,dt = \int\frac{1}{\chi_i}\,d\chi_i$$

$$-\frac{iE_i t}{\hbar} = \ln\left(\chi_i\right) + (\text{constant})$$

$$\chi_i = e^{-iE_i t/\hbar + \phi}$$

and so

$$\Psi_i = \Phi_i e^{-iE_i t/\hbar}$$

(b) **What is the "link" (in words; you need not derive this—I want to see if you understand this, so I am looking for a *concept*) between this result and the characteristic frequency of transition from an initial state described with $\Psi_i\left(r_1,\dots,r_N;R_1,\dots,R_P;t\right)$ to a final state described with, $\Psi_f\left(r_1,\dots,r_N;R_1,\dots,R_P;t\right)$.**

The link is that the excitation frequency is $\omega_{fi} = \dfrac{E_f - E_i}{\hbar}$. The picture is that a molecule in an isolated state is oscillating with frequency $E_i/\hbar$ since

$$e^{-iE_i t/\hbar} = \cos\left(E_i t/\hbar\right) - i\sin\left(E_i t/\hbar\right)$$

The final state is oscillating with the faster (if $E_f > E_i$) frequency, $E_f/\hbar$. In order to "boost" the electron from one state to another one, oscillating more quickly, we must add an oscillation with the frequency of the difference in frequencies between the two states. Thus, transitions only occur if the light has frequency at (or near) $\omega_{fi} = \dfrac{E_f - E_i}{\hbar}$.

7.   The Spin-Orbit Hamiltonian

We usually considered ignored spin-orbit interactions in this course. The standard way to approximate the effects of the spin-orbit interaction is to add an extra, "spin-orbit" term to the atomic Hamiltonian, $\hat{H}_{atom}$, giving the "full" Hamiltonian

$$\hat{H}_{SO} = \hat{H}_{atom} + \frac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right).$$

The first term is just the usual Hamiltonian for the atom (without including spin-orbit effects), which we know commutes with $\hat{J}^2$, so $\left[\hat{H}_{atom},\hat{J}^2\right]=0$.

(a) Why is the spin-orbit interaction usually negligible? When do you expect it to not be negligible?

In general, the electron is moving *much* slower than the speed of light, so that $\frac{|L|}{c^2}$ is a very tiny number and the spin-orbit correction is small. However, for atoms well down the periodic table (especially Actinides and 3rd row transition metals), the "core" electrons are moving very rapidly and spin-orbit effects are not entirely negligible.

(b) Show that J is a "good quantum number" for the spin-orbit Hamiltonian. That is, show that we can choose the eigenfunctions of $\hat{H}_{SO}$ so that they are also eigenfunctions of $\hat{J}^2$.

If J is a good quantum number, then $\left[\hat{H}_{SO},\hat{J}^2\right]=0$. To show this, we have that

$$
\begin{aligned}
\left[\hat{H}_{SO},\hat{J}^2\right] &= \left[\hat{H}_{atom}+\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\hat{J}^2\right]\\
&= \left[\hat{H}_{atom},\hat{J}^2\right]+\left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\hat{J}^2\right]\\
&= 0+\left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\right]\\
&= \left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\hat{L}^2+\hat{S}^2+2\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right]\\
&= \left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\hat{L}^2\right]+\left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),\hat{S}^2\right]+\left[\tfrac{Z}{2c^2 r^3}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right),2\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right]\\
&= \tfrac{Z}{2c^2 r^3}\hat{\boldsymbol{L}}\cdot\left[\hat{\boldsymbol{S}},\hat{L}^2\right]+\left[\tfrac{Z}{2c^2 r^3}\hat{\boldsymbol{L}},\hat{L}^2\right]\cdot\hat{\boldsymbol{S}}+\tfrac{Z}{2c^2 r^3}\hat{\boldsymbol{L}}\cdot\left[\hat{\boldsymbol{S}},\hat{S}^2\right]+\left[\tfrac{Z}{2c^2 r^3}\hat{\boldsymbol{L}},\hat{S}^2\right]\cdot\hat{\boldsymbol{S}}+0\\
&= 0+0+0+0\\
&= 0
\end{aligned}
$$

The key is to remember that

$$
\begin{aligned}
\left[\hat{L}^2,\hat{S}_{x,y,z}\right]&=0\\
\left[\hat{S}^2,\hat{S}_{x,y,z}\right]&=0\\
\left[\hat{L}^2,\hat{L}_{x,y,z}\right]&=0\\
\left[\hat{S}^2,\hat{L}_{x,y,z}\right]&=0
\end{aligned}
$$

and that every operator commutes with itself. We have also used the rule

$$\left[\hat{A}\hat{B},\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{A}\left[\hat{B},\hat{C}\right].$$

8.   The Kohn-Sham Equations.
The Kohn-Sham equations are derived by finding the "effective potential" such that the ground state electron density of the Kohn-Sham Hamiltonian

$$\hat{H}_{KS} = \sum_{i=1}^{N}\left(-\tfrac{\nabla_i^2}{2} + v\left(\boldsymbol{r}_i\right) + v_J\left[\rho;\boldsymbol{r}_i\right] + v_{xc}\left[\rho;\boldsymbol{r}_i\right]\right)$$

and the ground state density of the "real" molecular Hamiltonian

$$\hat{H}_{true} = \sum_{i=1}^{N}\left(-\tfrac{\nabla_i^2}{2} + v\left(\boldsymbol{r}_i\right)\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|}$$

are the same. By $v_J\left[\rho;\boldsymbol{r}\right]$ and $v_{xc}\left[\rho;\boldsymbol{r}\right]$ we denote that the Coulomb (v_J) and exchange-correlation (v_{xc}) potentials depend on the electron density. Using separation of variables on the Kohn-Sham Hamiltonian, we derive the Kohn-Sham equations for the Kohn-Sham orbitals and orbital energies,

$$\left\{\left(-\tfrac{\nabla^2}{2} + v\left(\boldsymbol{r}\right) + v_J\left[\rho;\boldsymbol{r}\right] + v_{xc}\left[\rho;\boldsymbol{r}\right]\right)\psi_\alpha\left(\boldsymbol{r}\right) = \varepsilon_\alpha\psi_\alpha\left(\boldsymbol{r}\right)\right\}_{\alpha=1}^{N}.$$

The electron density is determined by the orbitals using the equation

$$\rho\left(\boldsymbol{r}\right) = \sum_{\alpha=1}^{N}\left|\psi_\alpha\left(\boldsymbol{r}\right)\right|^2$$

(a)   We said that the Kohn-Sham Hamiltonian was a "mean field" or "independent-particle" model. What does this say about the interpretation of $v_J\left(\boldsymbol{r}\right) + v_{xc}\left(\boldsymbol{r}\right)$?

The idea of a "mean field" model is that the electrons do not feel each other individually. Rather, each electron feels an "average force" due to the other electrons. The potential, $v_J\left(\boldsymbol{r}\right) + v_{xc}\left(\boldsymbol{r}\right)$, takes the place of the electron-electron repulsion potential in the Hamiltonian, so it "stands in" for the electron-electron repulsion. That is, it is the "potential of mean force"—it models the "average potential" an electron feels at a point due to the other electrons.

(b)   One has to solve the Kohn-Sham equations to "self-consistency." Explain what this means and how the solution is constructed.

Self-consistency means that because the Kohn-Sham Hamiltonian depends on the Kohn-Sham orbitals (through the density), we have a nonlinear equation: the orbitals "put into the equation" must equal the ones taken out; otherwise we have two values for the same orbital, which is clearly not consistent.

One way to solve this is by fixed-point iteration.

1. Take an initial guess for the electron density, $\rho_0\left(\boldsymbol{r}\right)$. Substitute this in for $\rho_i\left(\boldsymbol{r}\right)$ in step 2 (below).

2. Compute $v_J[\rho_i; \boldsymbol{r}]$ and $v_{xc}[\rho_i; \boldsymbol{r}]$.

3. Solve the Kohn-Sham equations for $\rho_i(\boldsymbol{r})$. You will get out a set of orbitals, $\{\psi_\alpha[\rho_i; \boldsymbol{z}]\}_{\alpha=1}^N$.

4. Compute the electron density from these orbitals,

$$\rho_{i+1}(\boldsymbol{r}) = \sum_{\alpha=1}^N |\psi_\alpha[\rho_i; \boldsymbol{r}]|^2 .$$

5. If $\rho_{i+1}(\boldsymbol{r}) = \rho_i(\boldsymbol{r})$ (or it is at least close enough), the equation is self-consistent and we can stop. If not, go to step 2, and replace $\rho_i(\boldsymbol{r})$ with $\rho_{i+1}(\boldsymbol{r})$.

9. **Derive Koopmans' theorem for electron removal from a Hartree-Fock determinant.**
   For a Slater determinant, $|\psi_1 \ldots \psi_N|$, the energy formula is

   $$E = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(J_{ij} - K_{ij} \right)$$

   and the orbital energy of the αth orbital is

   $$\varepsilon_\alpha = h_\alpha + \sum_{i=1}^{N} \left(J_{i\alpha} - K_{i\alpha} \right)$$

(a) **Derive an expression for the change in energy between the neutral system (modeled with the Slater determinant $|\psi_1 \ldots \psi_N|$) and the cation modeled by removing the orbital, ψ_α, from the Slater determinant to form the $N-1$ electron state, $|\psi_1 \ldots \psi_{\alpha-1} \psi_{\alpha+1} \psi_{\alpha+2} \ldots \psi_N|$. Write the expression you obtain in terms of the orbital energy for the αth orbital.**

$$I_i \approx E\left[|\psi_1 \ldots \psi_{\alpha-1}\psi_{\alpha+1}\psi_{\alpha+2} \ldots \psi_N|\right] - E_{HF}\left[|\psi_1 \ldots \psi_N|\right]$$

$$\approx \sum_{\substack{k=1 \\ k \neq \alpha}}^{N} h_k + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq \alpha}}^{N} \sum_{\substack{l=1 \\ l \neq \alpha}}^{N} \left(J_{kl} - K_{kl} \right) - \left(\sum_{k=1}^{N} h_k + \frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} \left(J_{kl} - K_{kl} \right) \right)$$

$$= \left(-h_\alpha - \frac{1}{2} \sum_{\substack{k=1 \\ k \neq \alpha}}^{N} \left(J_{k\alpha} - K_{k\alpha} \right) - \frac{1}{2} \sum_{\substack{l=1 \\ l \neq \alpha}}^{N} \left(J_{\alpha l} - K_{\alpha l} \right) - \left(J_{\alpha\alpha} - K_{\alpha\alpha} \right) \right)$$

$$= - \left(h_\alpha + \sum_{\substack{k=1 \\ k \neq i}}^{N} \left(J_{k\alpha} - K_{k\alpha} \right) \right) - 0$$

$$= -\varepsilon_\alpha$$

(b) **What does this result have to do with the "chemical" interpretation of the Hartree-Fock orbitals and their orbital energies?**

The Hartree-Fock orbitals represent the orbitals from which electrons are removed to form cations. Thus, for example, the HOMO orbital in HF theory indicates how a molecule would prefer to "donate" an electron (it will be large near the most basic sites in the molecule) and the HOMO orbital energy is associated with the basicity of the molecule.

(c) **Koopmans' Theorem approximates the ionization potential with the negative of the orbital energy,**

$$IP \approx IP_{Koopmans'} \equiv -\varepsilon_N.$$

We could also approximate the ionization potential by subtracting the Hartree-Fock energy of the neutral molecule from the Hartree-Fock energy of the cation,

$$IP \approx IP_{HF} \equiv E_{HF}^{cation} - E_{HF}^{neutral}$$

Is IP_{HF} less than or grater than $IP_{Koopmans'}$? Why?

$IP_{HF} < IP_{Koopmans'}$ because $E_{HF}^{cation} < E\left[|\psi_1 \ldots \psi_{N-1}|\right]$. This latter inequality is associated with orbital relaxation: the actual Hartree-Fock (= lowest energy) orbitals of the cation are not the same as those in the neutral molecule because when we remove an electron from the original molecule, the other electrons feel less repulsion and "move toward the nucleus." Said differently, the Hartree-Fock orbitals for the neutral atom do not solve the Hartree-Fock equation for the cation.

10. **The Hohenberg-Kohn theorem states that the electron density can be used to determine all properties of any electronic system, that is, all properties of any system with a Hamiltonian of the form**

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} + v\left(r_i\right)\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|r_i - r_j\right|}$$

where $v(r)$ is any "well-behaved" function.

(a,b) **Prove the Hohenberg-Kohn Theorem**

The key idea behind the Hohenberg-Kohn theorem is that if you can never have two Hamiltonians with the same electron density, then the electron density determines the Hamiltonian. If the electron density determines the Hamiltonian, you can find the wave function by solving Schrödinger's equation. You can determine any property of the system from its wave function.

So, how do we show this? Well, we start with two Hamiltonians,

$$\hat{H}_1 = \hat{F} + \sum_{i=1}^{N} v_1\left(r_i\right)$$
$$\hat{H}_2 = \hat{F} + \sum_{i=1}^{N} v_2\left(r_i\right)$$

Here $\hat{F} = \sum_{i=1}^{N}\frac{-\nabla_i^2}{2} + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|r_i - r_j\right|}$. Denote the ground state wave functions for these Hamiltonians as Ψ_1 and Ψ_2, respectively. Then, regarding Ψ_2 as an approximate wave function for $\hat{H}_1$, we have

$$E_1 = \left\langle \Psi_1 \left| \hat{H}_1 \right| \Psi_1 \right\rangle < \left\langle \Psi_2 \left| \hat{H}_1 \right| \Psi_2 \right\rangle$$
$$\left\langle \Psi_1 \left| \hat{F} + \sum_{i=1}^{N} v_1\left(r_i\right) \right| \Psi_1 \right\rangle < \left\langle \Psi_2 \left| \hat{F} + \sum_{i=1}^{N} v_1\left(r_i\right) \right| \Psi_2 \right\rangle$$
$$\left\langle \Psi_1 \left| \hat{F} \right| \Psi_1 \right\rangle + \left\langle \Psi_1 \left| \sum_{i=1}^{N} v_1\left(r_i\right) \right| \Psi_1 \right\rangle < \left\langle \Psi_2 \left| \hat{F} \right| \Psi_2 \right\rangle + \left\langle \Psi_2 \left| \sum_{i=1}^{N} v_1\left(r_i\right) \right| \Psi_2 \right\rangle$$
$$\left\langle \Psi_1 \left| \hat{F} \right| \Psi_1 \right\rangle + \int \rho_1\left(r\right) v_1\left(r\right) dr < \left\langle \Psi_2 \left| \hat{F} \right| \Psi_2 \right\rangle + \int \rho_2\left(r\right) v_1\left(r\right) dr$$

We can derive the corresponding formula for $\hat{H}_2$ by simply interchanging "1" and "2" everywhere in the preceding equation. We obtain

$$\left\langle \Psi_2 \left| \hat{F} \right| \Psi_2 \right\rangle + \int \rho_2\left(r\right) v_2\left(r\right) dr < \left\langle \Psi_1 \left| \hat{F} \right| \Psi_1 \right\rangle + \int \rho_1\left(r\right) v_2\left(r\right) dr .$$

Adding these last two equations together, we get

$$\left\langle \Psi_1 \left| \hat{F} \right| \Psi_1 \right\rangle + \int \rho_1(\boldsymbol{r}) \, v_1(\boldsymbol{r}) \, d\boldsymbol{r} + \left\langle \Psi_2 \left| \hat{F} \right| \Psi_2 \right\rangle + \int \rho_2(\boldsymbol{r}) \, v_2(\boldsymbol{r}) \, d\boldsymbol{r}$$

$$< \left\langle \Psi_2 \left| \hat{F} \right| \Psi_2 \right\rangle + \int \rho_2(\boldsymbol{r}) \, v_1(\boldsymbol{r}) \, d\boldsymbol{r} + \left\langle \Psi_1 \left| \hat{F} \right| \Psi_1 \right\rangle + \int \rho_1(\boldsymbol{r}) \, v_2(\boldsymbol{r}) \, d\boldsymbol{r}$$

$$\int \rho_1(\boldsymbol{r}) \, v_1(\boldsymbol{r}) \, d\boldsymbol{r} + \int \rho_2(\boldsymbol{r}) \, v_2(\boldsymbol{r}) \, d\boldsymbol{r} < \int \rho_2(\boldsymbol{r}) \, v_1(\boldsymbol{r}) \, d\boldsymbol{r} + \int \rho_1(\boldsymbol{r}) \, v_2(\boldsymbol{r}) \, d\boldsymbol{r}$$

$$\int \left(\rho_1(\boldsymbol{r}) - \rho_2(\boldsymbol{r}) \right) \left(v_1(\boldsymbol{r}) - v_2(\boldsymbol{r}) \right) d\boldsymbol{r} < 0$$

Now, we have that $v_1(\boldsymbol{r}) \neq v_2(\boldsymbol{r})$, by assumption. If, by some chance, $\rho_1(\boldsymbol{r}) = \rho_2(\boldsymbol{r})$, then the inequality above would be violated (the answer would be zero, not less than zero). So the same density can never correspond to two Hamiltonians. This means that there is an unambiguous way to determine the Hamiltonian (ergo the wave function, ergo everything) from the density.

Part 2. Multiple-Choice; Short Answer (1 point each; 25 points total.) Starred questions were different on the second final, but should be easy enough to figure out.

1.* Number the following units in order of *increasing* energy

__4__ 1 Hartree   __1__ 1 Hertz   __3__ 1 kJ/mol   __2__ 1 cm^{-1}

2.* Number the following units in order of *increasing* distance

__1__ 1 Bohr   __2__ 1 Angstrom   __3__ 1 nanometer

3. There has been much recent interest in "exotic" analogues of the hydrogen atom, wherein the electron is replaced by another species. The most popular choice is the muon, which has the same charge as the electron but weighs 207 times more. Assuming the Born-Oppenheimer approximation holds, what are the energy levels of the muon in the presence of an atomic nucleus with charge Z. Express your answer in Hartree units.

$$E_n^\mu \equiv -\frac{207 \cdot Z^2}{2n^2}$$

In the next few problems, we will consider Slater determinants for the Lithium atom with electron configuration $1s^2 2s^1$ and $M_S = \frac{1}{2}$.

4. Write a Slater determinant appropriate for a *restricted* Hartree-Fock (RHF) approximation. (Do not use the shorthand notation.)

$$\Psi_{Li}^{RHF} = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{1s}(r_1)\alpha(1) & \psi_{1s}(r_1)\beta(1) & \psi_{2s}(r_1)\alpha(1) \\ \psi_{1s}(r_2)\alpha(2) & \psi_{1s}(r_2)\beta(2) & \psi_{2s}(r_2)\alpha(2) \\ \psi_{1s}(r_3)\alpha(3) & \psi_{1s}(r_3)\beta(3) & \psi_{2s}(r_3)\alpha(3) \end{vmatrix}$$

5. Write a Slater determinant appropriate for an *unrestricted* Hartree-Fock (UHF) approximation. (You can use the shorthand notation.)

$$\Psi_{Li}^{RHF} = \begin{vmatrix} \psi_{1s}^{(\alpha)}\alpha & \psi_{1s}^{(\beta)}\beta & \psi_{2s}^{(\alpha)}\alpha \end{vmatrix}$$

6. Is the RHF wave function from part 4 an eigenfunction of

$\hat{S}^2$	**Yes**	No
$\hat{L}^2$	**Yes**	No

7. Is the UHF wave function from part 5 an eigenfunction of

$\hat{S}^2$	Yes	**No**
$\hat{L}^2$	**Yes**	No

Suppose we perform the Hartree-Fock procedure for a molecule, finding the molecular orbitals that minimize the energy.

8. True or False. For B_2, the unrestricted Hartree Fock energy is strictly less than the restricted Hartree-Fock energy. ($E_{UHF} < E_{RHF}$)

    (a) True   (b) False

9. True or False. For C_2, the unrestricted Hartree Fock energy is strictly less than the restricted Hartree-Fock energy. ($E_{UHF} < E_{RHF}$)

    (a) True   **(b) False**

10,11. For each of the following operators, if the Slater determinant $\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right|$ is an eigenfunction of the operator, fill in its eigenvalue. Otherwise, write in "not an eigenvalue." Use SI units.

$$\hat{L}^2\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right| = 2\hbar^2\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right|$$

$$\hat{S}^2\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right| = \tfrac{3}{4}\hbar^2\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right|$$

$$\hat{S}_z\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right| = \hbar\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right|$$

$$\hat{J}_z\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right| = \tfrac{3}{2}\hbar\left|\psi_{2p_1}\alpha \quad \psi_{2p_0}\alpha\right|$$

12. Which of the following operators commute with $\hat{J}_x$. (There may be more than one answer.)

(a) $\hat{J}^2$ **(d)** $\hat{L}_x$ **(g)** $\hat{S}_x$ **(j)** $\hat{J}_x$

(b) $\hat{S}^2$ (e) $\hat{L}_y$ (h) $\hat{S}_y$ (k) $\hat{J}_y$
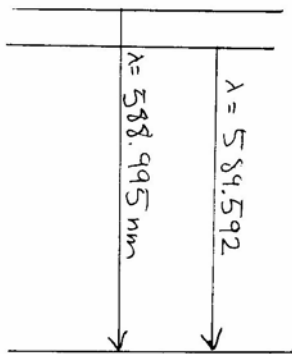
(c) $\hat{L}^2$ (f) $\hat{L}_z$ (i) $\hat{S}_z$ (l) $\hat{J}_z$

13. Back when I pretended to be a physicist, I would often calibrate a spectrometer using the emission from the sodium "D" line (where "D" stands for "doublet" in typically confused physics parlance). The sodium "D" line corresponds to the $1s^2 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^6 3s^1$ transition. Use term symbols to label the states on the energy level diagram.

Term Symbol

The highest-energy state is $^2P_{3/2}$. The next state is $^2P_{1/2}$.

The ground state is $^2S_{1/2}$

$\lambda = 588.995$ nm

$\lambda = 589.592$

14.* If you want to determine the important resonance structures for a molecule, you should use
(a) valence bond theory   (b) molecular orbital theory.

15. If you want to determine the dissociation energy for a molecule with a simple model, you should use
(a) valence bond theory   (b) molecular orbital theory.

You are using absorption spectroscopy to measure the concentration of pollutants in the flue gas of one of the big Hamilton smoke-stacks.

16. Since the temperature is high but the pressure is relatively low, you expect the line shape to be
(a) Gaussian   (b) Lorentzian

17. Appalled at what you see, you recommend that the industry runs the exhaust through a "scrubber," where the gas is still at the *same* high temperature, but the pressure of the gas is *increased* a little bit. The full-width at half-maximum of the line will
(a) decrease   (b) increase

18,19. For each type of broadening, there was a characteristic line shape. The width of the line was usually measured using the full-width at half-maximum, Γ, but it is sometimes more convenient to express results in terms of the half-width and half-maximum, $\gamma = \frac{\Gamma}{2}$. Corresponding to each of the following line shapes, write the formula for the lineshape and whether it is associated with inhomogeneous or homogeneous broadening. When you need a proportionality constant, use κ.

Type of Line Shape	Formula for Line Shape	Type of Broadening
Gaussian	$\frac{\kappa_1}{\gamma} e^{-\kappa_2 \left(\frac{\omega - \omega_0}{\gamma}\right)^2}$	Inhomogeneous
Lorentzian	$\frac{\kappa \cdot \gamma}{\gamma^2 + (\omega - w_0)^2}$	Homogeneous

Name:

20. Two **3d** orbitals can combine to form a σ_g^+ molecular orbital. **Write the form of this molecular orbital.**

$$\psi_{\sigma_g(3d)}(\boldsymbol{r}) = \psi_{3d_{z^2}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{z^2}}^{(r)}(\boldsymbol{r})$$

21. Two **3d** orbitals can combine to form a π_g^- molecular orbital. **Write the form of this molecular orbital.**

$$\psi_{\pi_g^-(3d)}(\boldsymbol{r}) = \psi_{3d_{yz}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{yz}}^{(r)}(\boldsymbol{r})$$

22. **Is the $\sigma_g^+ \rightarrow \pi_g^-$ transition allowed for forbidden?**

Forbidden.

23. **We said that Hartree-Fock calculations were unreliable whenever there was more than one important Slater determinant. (That is, whenever it was difficult to unambiguously assign electrons to orbitals, so that the "orbital-model" of a molecule breaks down.) Which of the following types of calculations would be appropriate in this case.**
(a) Configuration Interaction with single and double excitations (CISD)
(b) Configuration Interaction with single, double, triple, and quadruple excitations (CISDTQ)
(c) Multi-reference singles and doubles configuration interaction (MRSDCI; MRCISD)
(d) Moller-Plesset Perturbation theory at second order (MP2; MBPT2)
(e) Coupled-Cluster Calculations with singles and doubles (CCSD)
(f) Coupled-Cluster Calculations with singles, doubles, triples, and quadruples (CCSDTQ)
(g) Full Configuration Interaction Calculations (Full-CI)

24. **Which method is better for anions:**
(a) Many-Body Perturbation Theory Calculations   **(b) Couple-Cluster Calculations**

25. **Which method can be thought of as taking the form of a configuration-interaction calculation with single and double excitations (CISD) and then generalizing the form to "guess" the coefficients of triple, quadruple, and higher-order excitations?**
  (a) density-functional theory
  (b) coupled-cluster theory with single and double excitations (CCSD)
  (c) coupled-cluster theory with single, double, triple, and quadruple excitations (CCSDTQ)
  (d) Configuration Interaction with singles, doubles, triples, and quadruples (CISDTQ)
  (e) Full-Configuration Interaction (Full-CI)

Name:

Part 3.   Thinking Problems (30 Points; 3 points each)

1. **For atoms, it is observed that the electron density is almost piecewise exponential—at different distances from the nucleus the electron density decays at different exponential rates. You may wish to recall that the electron density can be written as a sum of "Kohn-Sham" orbitals,**

$$\rho(\boldsymbol{r}) = \sum_{\alpha} |\psi_{\alpha}(\boldsymbol{r})|^2$$

In the figure on the next page, we plot the logarithmic derivative of the density

$$\frac{d\ln(\rho(r))}{dr}$$

against the axis for Cobalt ($Z = 27$). The next page has the figure for some atoms in the 4-electron isoelectronic series.

(a) **Explain the interpretation of these results. Be sure to make it clear that you understand the significance of the logarithmic derivative.**

The significance of the logarithmic derivative is that it captures the rate of exponential decay. Specifically,

$$\frac{d\ln(e^{-\zeta r})}{dr} = \frac{d(-\zeta r)}{dr} = -\zeta$$

Recall that all of the hydrogenic orbitals have a form like $e^{-Zr/n}$. We said that for many-electron atoms, the atomic number is replaced by an "effective nuclear charge." So, we can say that each orbital in an atom has an effective nuclear charge, and thus has a characteristic exponential decay. Let's write this as

$$\psi_i(\boldsymbol{r}) \sim e^{-\zeta_i r/n_i}$$

where ζ_i and n_i are the effective nuclear charge and principle quantum number, respectively, of the ith orbital. Obviously

$$|\psi_i(\boldsymbol{r})|^2 \sim e^{-2\zeta_i r/n_i}$$

and so when we form the density from orbitals, it will have logarithmic derivatives at different places, depending on what is the dominant orbital. We could write

$$\frac{d\ln(\rho(r))}{dr} = \frac{d\ln\left(\sum_{\alpha=1}^{N}|\psi_{\alpha}(\boldsymbol{r})|^2\right)}{dr} = \sum_{\alpha=1}^{N}\frac{d\ln|\psi_{\alpha}(\boldsymbol{r})|^2}{dr} \sim \sum_{\alpha=1}^{N}\left(\frac{-2\zeta_{\alpha}}{n_{\alpha}}\right)$$

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where the "dominate term" in the sum depends on how far you are away from the nucleus. Very close to the nucleus, we have 1s orbitals, so $n = 1$. Also, electrons very close to the nucleus are not screened, so $\zeta = Z$, where Z is the atomic number. The figures on the next pages confirm that, near the nucleus, $\frac{d\ln(\rho(r))}{dr} = -2Z$. Far from the nucleus, the effective nuclear charge is about 1 (for a neutral atom), and so we expect
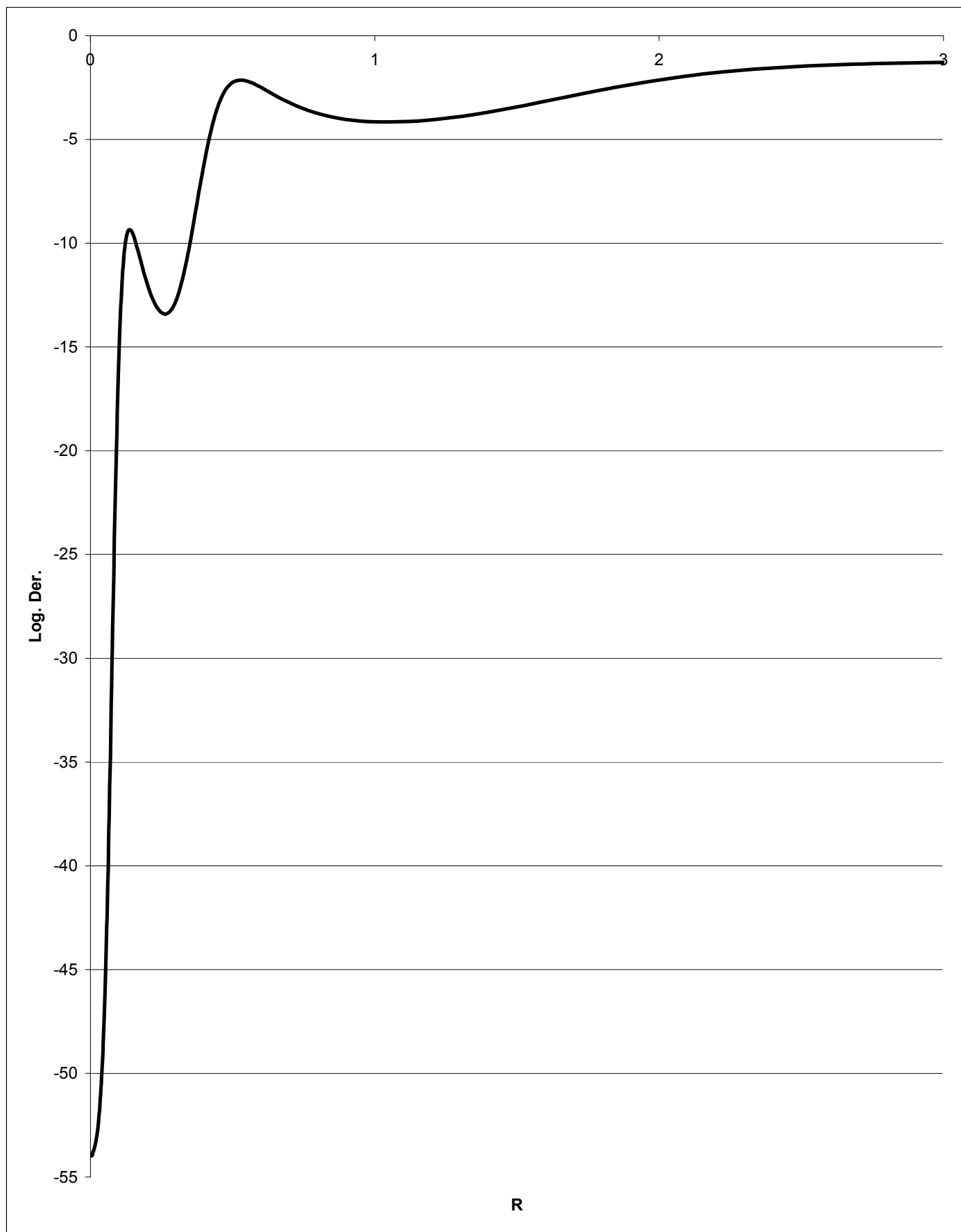
$$\frac{d\ln(\rho(r))}{dr} \sim \frac{-2}{n_{valence \atop electrons}} \sim 1 \qquad \text{(for Be)}$$

$$\sim \tfrac{-2}{3} \qquad \text{(for Co)}$$

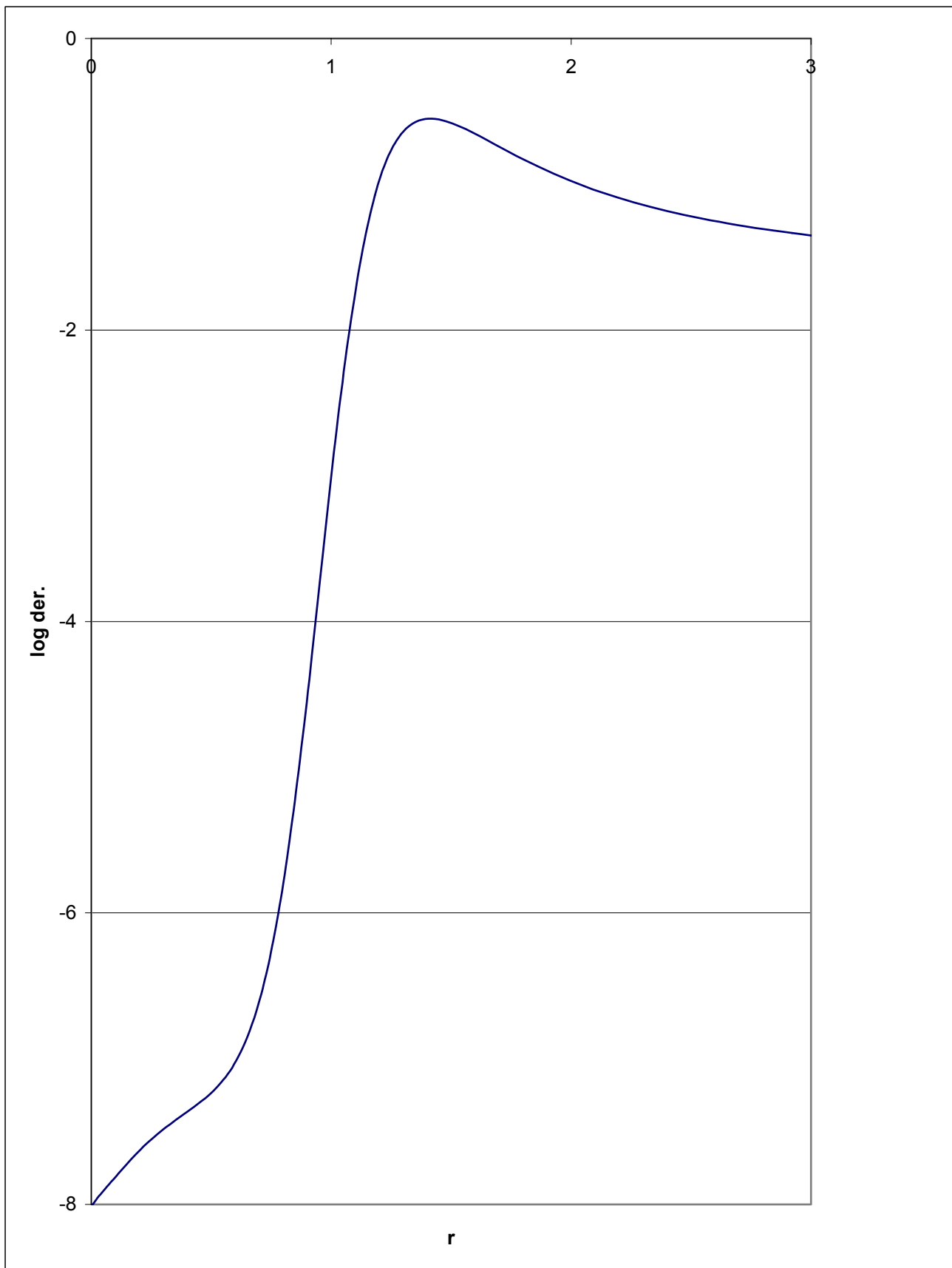These aren't perfect formulae, but they are pretty close.

In the intermediate regions you expect intermediate behavior. In Cobalt, for example, there is a clear indication of the 2s,2p shell—there is a "leveling off" and some "shell structure" around $\frac{2\zeta}{n} = -13$ and since $n = 2$, we can infer that the effective nuclear charge for the *2s* and *2p* electrons is around -13.

So, in just one sentence, the "significance" of these results is that these plots are related to the effective nuclear charge.

2. **Look at the figure on the next page. Look at the far right-hand side of the figure; notice that when the number of electrons is much smaller than the atomic number, orbitals with the same principle quantum number (e.g., the 3s, 3p, and 3d orbitals) have very similar energy.**

(a) Explain why this is so in words.

In words, when the atomic number is much larger than the number of electrons, the electrons attraction to the nucleus is a much larger term in the Hamiltonian than the electron-electron repulsion. Thus, electrons number one priority is to arrange themselves in an optimal way in the nucleus and, to a first approximation, the effects of electron-electron repulsion can be ignored. Since, in the absence of electron-electron repulsion, things look like the Hydrogenic atom, we expect that when the electron-electron repulsion is not-that-important, the orbitals act pseudo-hydrogenic.

(b) Note also that the energies are, in fact, very close to what we would expect for an atom without any electron-electron repulsion whatsoever. Derive an approximation to the orbital energies in highly charged many-electron atoms result by using a transformation of coordinates to rewrite the Hamiltonian for highly charged atoms as

$$\sum_{i=1}^{N}\left(-\frac{\nabla_{x_i}^2}{2} - \frac{1}{x_i}\right) + (\text{small perturbation})$$

We use the same transformation of coordinates we used to derive the $\frac{1}{Z}$ expansion in the second homework. Let $\boldsymbol{R}_i = Z\boldsymbol{r}_i$. Then

$$\frac{\partial^2}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial}{\partial X}\frac{\partial X}{\partial x}$$
$$= \left(\frac{\partial X}{\partial x}\right)^2 \frac{\partial^2}{\partial X^2}$$
$$= Z^2 \frac{\partial^2}{\partial X^2}$$

So we have that $\nabla_{r_i}^2 = Z^2 \nabla_{R_i}^2$. Similarly,

$$\frac{Z}{r_i} = \frac{Z^2}{R_i}$$
$$\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \frac{Z}{|\boldsymbol{R}_i - \boldsymbol{R}_j|}$$

Changing variables in the atomic Hamiltonian, then, we get that

$$\hat{H}_{atom} = \sum_{i=1}^{N}\left(-\frac{\nabla_{r_i}^2}{2} - \frac{Z}{r_i}\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|}$$

$$= \sum_{i=1}^{N}\left(-Z^2\frac{\nabla_{\boldsymbol{R}_i}^2}{2} - \frac{Z^2}{R_i}\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{Z}{\left|\boldsymbol{R}_i - \boldsymbol{R}_j\right|}$$

Writing the Schrödinger equation in the new variables, we have that

$$\left[\sum_{i=1}^{N}\left(-Z^2\frac{\nabla_{\boldsymbol{R}_i}^2}{2} - \frac{Z^2}{R_i}\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{Z}{\left|\boldsymbol{R}_i - \boldsymbol{R}_j\right|}\right]\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right) = E\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right)$$

$$\left[\sum_{i=1}^{N}\left(-\frac{\nabla_{\boldsymbol{R}_i}^2}{2} - \frac{1}{R_i}\right) + \frac{1}{Z}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{R}_i - \boldsymbol{R}_j\right|}\right]\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right) = \frac{E}{Z^2}\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right) \quad (1)$$

$$\left[\sum_{i=1}^{N}\left(-\frac{\nabla_{\boldsymbol{R}_i}^2}{2} - \frac{1}{R_i}\right) + \frac{1}{Z}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{R}_i - \boldsymbol{R}_j\right|}\right]\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right) = \mathcal{E}_Z\Psi\left(\boldsymbol{R}_1,...,\boldsymbol{R}_N\right)$$

If Z is very large, the last term is small. However, there are a lot of electron-electron repulsion terms, and the *sum* of all the terms will be substantial unless $Z \gg N$, in which case the electron-nuclear attraction will clearly be dominant. In this case, you can—to a first approximation— ignore the electron-electron repulsion term. The resulting expression is just the Schrödinger equation for the Hydrogen atom, and the solutions are the Hydrogenic orbitals (scaled by Z) and the Hydrogenic orbital energies (scaled by Z^2). One could make further corrections using perturbation theory.
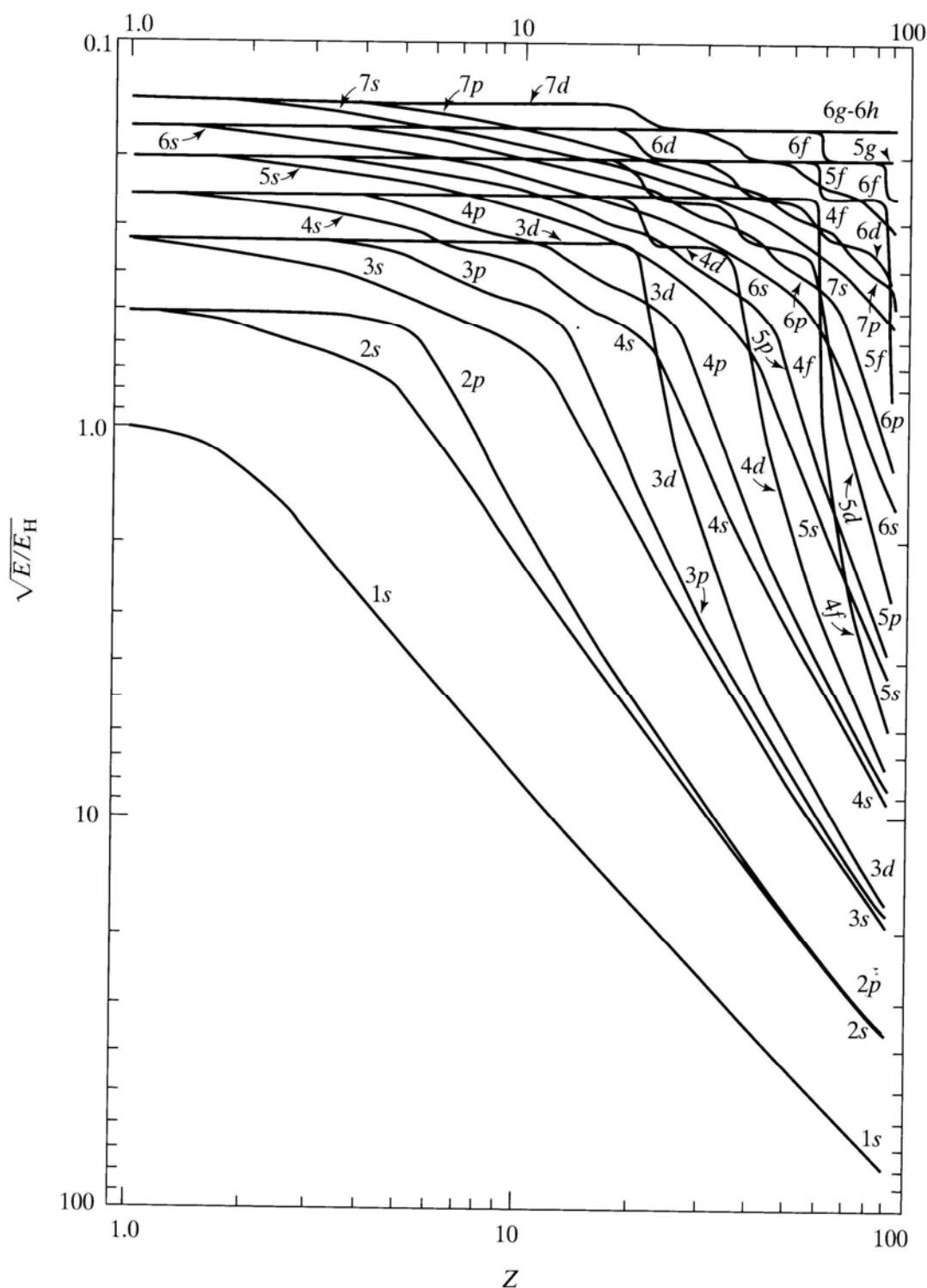
FIGURE 11.2 Atomic-orbital energies as a function of atomic number for neutral atoms, as calculated by Latter. [Figure redrawn by M. Kasha from R. Latter, *Phys. Rev.*, **99**, 510 (1955). Used by permission.] Note the logarithmic scales. E_H is the ground-state hydrogen-atom energy, -13.6 eV.

3. **Parriser's Approximation, electronegativity, and chemical hardness.**
   The energy of an atom or molecule can be written in the form

$$E_0\left(N_0\right) \equiv \left\langle \Psi_0\left(N_0\right) \middle| \sum_{i=1}^{N_0}\left[-\tfrac{\nabla_i^2}{2} + v_0\left(r_i\right)\right] + \sum_{j=i+1}^{N_0}\sum_{i=1}^{N_0}\tfrac{1}{|r_i-r_j|} \middle| \Psi_0\left(N_0\right)\right\rangle$$

   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

$$h\left(N_0\right) \equiv \left\langle \Psi_0\left(N_0\right) \middle| -\tfrac{\nabla_1^2}{2} + v_0\left(r_1\right) \middle| \Psi_0\left(N_0\right)\right\rangle$$

$$v_{ee}\left(N_0\right) \equiv \left\langle \Psi_0\left(N_0\right) \middle| \tfrac{1}{|r_2-r_1|} \middle| \Psi_0\left(N_0\right)\right\rangle$$

(a) **Show that the energy can be written as**

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

Using the fact that electrons are identical particles, we must have that

$$\left\langle \Psi_0\left(N_0\right) \middle| \tfrac{-\nabla_i^2}{2} + v_0\left(r_i\right) \middle| \Psi_0\left(N_0\right)\right\rangle = \left\langle \Psi_0\left(N_0\right) \middle| \tfrac{-\nabla_j^2}{2} + v_0\left(r_j\right) \middle| \Psi_0\left(N_0\right)\right\rangle = h\left(N_0\right)$$

for all i and j. Similarly, we must have that

$$\left\langle \Psi_0\left(N_0\right) \middle| \tfrac{1}{\|r_i-r_j\|} \middle| \Psi_0\left(N_0\right)\right\rangle = \left\langle \Psi_0\left(N_0\right) \middle| \tfrac{1}{\|r_{i'}-r_{j'}\|} \middle| \Psi_0\left(N_0\right)\right\rangle = v_{ee}\left(N_0\right)$$

Thus, we have that

$$E_0\left(N_0\right) \equiv \left\langle \Psi_0\left(N_0\right) \middle| \sum_{i=1}^{N_0}\left[-\tfrac{\nabla_i^2}{2} + v_0\left(r_i\right)\right] + \sum_{j=i+1}^{N_0}\sum_{i=1}^{N_0}\tfrac{1}{|r_i-r_j|} \middle| \Psi_0\left(N_0\right)\right\rangle$$

$$= \sum_{i=1}^{N_0}\left\langle \Psi_0\left(N_0\right) \middle| -\tfrac{\nabla_i^2}{2} + v_0\left(r_i\right) \middle| \Psi_0\left(N_0\right)\right\rangle + \sum_{j=i+1}^{N_0}\sum_{i=1}^{N_0}\left\langle \Psi_0\left(N_0\right) \middle| \tfrac{1}{|r_i-r_j|} \middle| \Psi_0\left(N_0\right)\right\rangle$$

$$= \sum_{i=1}^{N_0}h\left(N_0\right) + \sum_{j=i+1}^{N_0}\sum_{i=1}^{N_0}v_{ee}\left(N_0\right)$$

$$= h\left(N_0\right)\sum_{i=1}^{N_0}1 + v_{ee}\left(N_0\right)\sum_{j=i+1}^{N_0}\sum_{i=1}^{N_0}1$$

$$= N_0 h\left(N_0\right) + \left(\tfrac{N_0(N_0-1)}{2}\right)v_{ee}\left(N_0\right)$$

It is a surprisingly good assumption to assume that $h(N_0)$ and $v_{ee}(N_0)$ are *constant*—they do not depend on the number of electrons. That is, the primary effect of adding electrons to the system is the additional kinetic energy, electron-nuclear attraction, and electron-electron repulsion terms in the Hamiltonian, and not the change in the wave function. In this case, the energy is a *quadratic* expression in the number of electrons. (Empirical data confirms that this is almost true.) If the energy is assumed to be quadratic, then we can write

$$E(N) = E(N_0) + (N - N_0)\frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}(N - N_0)^2 \frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

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.

(b,c) Approximate $v_{ee}(N_0)$ and $h(N_0)$ using I and A. (The expression for $v_{ee}(N_0)$ 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. This led to so-called semiempirical approaches to quantum chemistry, the most widely used of which is the famous Pariser-Parr-Pople approximation.) [Hint: You may find it helpful to do parts d and e first, and then come back to this.]

The easiest way to do this is to first evaluate

$$\frac{\partial E}{\partial N}\Big|_{N=N_0} = h(N_0) + (N_0 - \tfrac{1}{2})v_{ee}(N_0)$$

$$\frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0} = v_{ee}(N_0)$$

These follow directly from differentiating our expression for the energy.

Next, note that

$$E(N_0 + 1) = E(N_0) + (1)\frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}(1)^2 \frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

$$E(N_0 - 1) = E(N_0) + (-1)\frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}(-1)^2 \frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

$$E(N_0 + 1) - E(N_0) = \frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}\frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

$$E(N_0 - 1) - E(N_0) = -\frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}\frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

$$-A = \frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}\frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

$$I = -\frac{\partial E}{\partial N}\Big|_{N=N_0} + \tfrac{1}{2}\frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0}$$

Adding the last two equations we get $v_{ee}(N_0) = \frac{\partial^2 E}{\partial N^2}\Big|_{N=N_0} = I - A$.

Subtracting the equation for I from that for $-A$ we get

$$\frac{\partial E}{\partial N}\Big|_{N=N_0} = -\frac{I + A}{2}$$

Combining these, we get

$$-\frac{(I+A)}{2} = h\left(N_0\right) + \left(N_0 - \tfrac{1}{2}\right) v_{ee}\left(N_0\right)$$
$$-\frac{(I+A)}{2} = h\left(N_0\right) + \left(N_0 - \tfrac{1}{2}\right)(I - A)$$
$$h\left(N_0\right) = \left(\tfrac{-1}{2} - \left(N_0 - \tfrac{1}{2}\right)\right) I + \left(-\tfrac{1}{2} + \left(N_0 - \tfrac{1}{2}\right)\right) A$$
$$h\left(N_0\right) = -N_0 I + \left(N_0 - 1\right) A$$
$$h\left(N_0\right) = -I - \left(N_0 - 1\right)(I - A)$$
$$h\left(N_0\right) = -N_0\left(I - A\right) - A$$

(d) **The quantity** $\mu = \frac{\partial E}{\partial N}\big|_{N=N_0}$ **is called the electronic chemical potential (for obvious reasons). The electronic chemical potential is the negative of the Mulliken electronegativity,**

$$\mu = -\chi_{Mulliken}$$

Explain why $\frac{\partial E}{\partial N}\big|_{N=N_0}$ **should measure electronegativity and write** μ **in terms of** I **and** A **.**

$\frac{\partial E}{\partial N}\big|_{N_0}$ measures the energetic benefit of adding electrons to the atom. When $\frac{\partial E}{\partial N}\big|_{N_0}$ is large and negative, adding an electron is very favorable (it makes the energy go down a lot) and the electronegativity is high. When $\frac{\partial E}{\partial N}\big|_{N_0}$ is small, there is little benefit to gaining up electrons—and also little penalty from forfeiting electrons. Electrons are readily donated, in concord with the fact that the electronegativity is small.

From above, we know that

$$\mu = -\frac{I+A}{2}$$

(e) **The quantity** $\eta = \frac{\partial^2 E}{\partial N^2}\big|_{N=N_0}$ **is called the Parr-Pearson chemical hardness. It is associated with the hard-soft acid-base principle, among other things. One often states that "small cations" are hard Lewis acids. Justify this using your result from part (b). Write** η **in terms of** I **and** A **.**

$\eta = I - A$ (from above). Also, $\eta = v_{ee}\left(N_0\right)$. For small cations, the electrons are "crammed together" into a smaller space, and so the electron-electron repulsion is greater. The hardness is also greater.

Name:

(f) **Using the data in the following table, compute the charge on the Lithium atom in** LiF **. We can approximate the energy of** LiF **as**

$$E_{LiF} = E_{Li}\left(N_{Li}\right) + E_F\left(N_F\right)$$

and we can approximate the energies of the Lithium and Fluorine atoms (for various numbers of electrons) using the results in parts (c) and (d) and the data in the following table.

Atom	μ (for neutral atom; in eV)	η (for neutral atom, in eV)
Li	-3.01	4.78
F	-10.41	14.02

So $N_{Li} = 3 - \Delta N$, $N_F = 9 + \Delta N$, where ΔN electrons are donated from Li to F.

One has, then, that

$$E_{Li}\left(3 - \Delta N\right) = E_{Li}\left(3\right) - \mu_{Li}\Delta N + \frac{(\Delta N)^2}{2}\eta_{Li}$$
$$E_F\left(9 + \Delta N\right) = E_F\left(9\right) + \mu_F\Delta N + \frac{(\Delta N)^2}{2}\eta_F$$

So

$$E_{LiF} = E_{Li}\left(N_{Li}\right) + E_F\left(N_F\right) = E_{Li}\left(3\right) - \mu_{Li}\Delta N + \frac{(\Delta N)^2}{2}\eta_{Li} + E_F\left(9\right) + \mu_F\Delta N + \frac{(\Delta N)^2}{2}\eta_F$$

To find the best value for ΔN, we minimize the energy with respect to ΔN.

So, we evaluate

$$0 = \frac{\partial E_{LiF}\left(\Delta N\right)}{\Delta N} = -\mu_{Li} + \mu_F + \eta_{Li}\Delta N + \eta_F\Delta N$$
$$\frac{\mu_{Li} - \mu_F}{\eta_{Li} + \eta_F} = \Delta N$$
$$.39 = \Delta N$$

The Lithium atom donates .39 electrons, then, and has a $+.39$ charge in this model.

Name:

4. **The density-matrix.**
One of the most useful quantities in quantum chemistry—especially for independent-particle models—is the first-order density matrix. For example, for the Hartree-Fock equations, the first-order density matrix is a specific sum of the Hartree-Fock orbitals,

$$\gamma_{HF}\left(z,z'\right) = \sum_{i=1}^{N} \psi_i^*\left(z\right)\psi_i\left(z'\right)$$

where, as before, $z = \left(r,\sigma\right)$ and $z' = \left(r',\sigma'\right)$ represent both space and spin coordinates of the electron.

(a) Show that the Hartree-Fock equations can be rewritten as a single equation for the density-matrix,

$$\left[-\frac{\nabla_r^2}{2} + v\left(r\right) + \int \frac{\gamma\left(z',z'\right)}{\left|r-r'\right|}dz'\right]\gamma\left(z,z'\right) - \int \frac{\left|\gamma\left(z',z\right)\right|^2}{\left|r-r'\right|}dz' = \left(\sum_{i=1}^{N}\varepsilon_i\right)\gamma\left(z,z'\right)$$

Because this is a nonlinear equation, it cannot (usually) be solved analytically, and iterative (e.g., self-consistent) methods of solution are required.

The Hartree-Fock Equations can be written as

$$\left[-\frac{\nabla^2}{2}+v\left(r\right)\right]\psi_\alpha\left(z\right) + \sum_{i=1}^{N}\int \frac{\left|\psi_i\left(z'\right)\right|^2}{\left|r'-r\right|}dr'\psi_\alpha\left(z\right) - \sum_{i=1}^{N}\int \frac{\psi_i^*\left(z'\right)\psi_\alpha\left(z'\right)}{\left|r'-r\right|}dr'\psi_i\left(z\right) = \varepsilon_\alpha\psi_\alpha\left(z\right)$$

$$\left[-\frac{\nabla^2}{2}+v\left(r\right)\right]\psi_\alpha\left(z\right) + \left[\int \frac{\sum_{i=1}^{N}\left|\psi_i\left(z'\right)\right|^2}{\left|r'-r\right|}dr'\right]\psi_\alpha\left(z\right) - \int \frac{\sum_{i=1}^{N}\psi_i^*\left(z'\right)\psi_i\left(z\right)\psi_\alpha\left(z'\right)}{\left|r'-r\right|}dr' = \varepsilon_\alpha\psi_\alpha\left(z\right)$$

$$\left[-\frac{\nabla^2}{2}+v\left(r\right)\right]\psi_\alpha\left(z\right) + \left[\int \frac{\gamma\left(z',z'\right)}{\left|r'-r\right|}dr'\right]\psi_\alpha\left(z\right) - \int \frac{\gamma\left(z,z'\right)\psi_\alpha\left(z'\right)}{\left|r'-r\right|}dr' = \varepsilon_\alpha\psi_\alpha\left(z\right)$$

Multiply on the left by $\psi_\alpha^*\left(x\right)$ and sum. We have

$$\left[-\frac{\nabla^2}{2}+v\left(r\right)\right]\psi_\alpha^*\left(x\right)\psi_\alpha\left(z\right) + \left[\int \frac{\gamma\left(z',z'\right)}{\left|r'-r\right|}dr'\right]\psi_\alpha^*\left(x\right)\psi_\alpha\left(z\right) - \psi_\alpha^*\left(x\right)\int \frac{\gamma\left(z,z'\right)\psi_\alpha\left(z'\right)}{\left|r'-r\right|}dr' = \varepsilon_\alpha\psi_\alpha^*\left(x\right)\psi_\alpha\left(z\right)$$

$$\left[-\frac{\nabla^2}{2}+v\left(r\right)+\int \frac{\gamma\left(z',z'\right)}{\left|r'-r\right|}dr'\right]\gamma\left(z,x\right) - \int \frac{\gamma\left(z,z'\right)\gamma\left(z',x\right)}{\left|r'-r\right|}dr' = \sum_{\alpha=1}^{N}\varepsilon_\alpha\psi_\alpha^*\left(x\right)\psi_\alpha\left(z\right)$$