Cornell University

Department of Physics

Phys 480/680, Astro 690 April 22, 2005

Computational Physics, Spring 2005

Homework Assignment # 9

(Due Thursday, April 28)

Agenda and readings for the weeks of May 4-7:

Goal: Predict bond length of H_2 molecule!

Readings marked NR are from *Numerical Recipes: The Art of Scientific Computing*, 2^{nd} edition (in C). Readings marked LN are from the course lecture notes to be found at http://www.ccmr.cornell.edu/~muchomas/P480.

Recap of last week of class:

- 04/19 Lec 22: Conjugate gradient algorithm
  Reading: 10.6
- 04/21 Lec 23: FFT
  Reading: 12.2
- 04/21 Lab 8: Finite difference test and numerical precision

Preview of final weeks of class:

- 04/26 Lec 24: Further optimizations for spectral methods; *ab initio* pseudopotentials
- 04/28 Lec 25: Go directly to lab
- 04/28 Lab 9: Performance of numerical minimization techniques (from Lab 8); quantum states of harmonic oscillator (Lab 7) and quantum dot (Lab 8), physics of hydrogen molecule (Lab 9)
- 05/03 Lec 26: DFT++ expressions for general case of variable fillings
  Reading: Secs. 1–4 of "New algebraic formulation of density functional calculation," by Sohrab Ismail-Beigi and T.A. Arias, Computer Physics Communications 128:1-2, 1-45 (June 2000). Preprint: http://arxiv.org/abs/cond-mat/9909130.
- 05/05 Lec 27: Extraction of eigenstates from variational principle
- 05/05 Lab 10: Electronic structure of crystalline germanium solid

Contents

1 Density functional calculation of molecules **2**
1.1 Nuclear-nuclear potential energy 2
1.2 Electron-nuclear potential (-Z/r) 2
1.2.1 Debugging 3
1.3 Hydrogen molecule 4

1 Density functional calculation of molecules

In this problem, you will use your software to evaluate the bond-length of the H_2 molecule directly from first principles using your own software.

1.1 Nuclear-nuclear potential energy

An important part of the energy of a molecule or solid is the potential energy between the nuclei

$$U_{nn} = \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J}{|\vec{r}_I - \vec{r}_J|}.$$

For us, this sum is somewhat tricky because we work in periodic boundary conditions and must sum over all of the the repeated copies of the nuclei. However, outside of a small Gaussian distribution of charge, the potential is identical to that of a point charge. Thus, we can calculate the energy of a periodic array of charges by solving for the electrostatic energy of Gaussian distributions as we did in Problem Set # 7.

To do this, make a new copy your program "poisson.m" called "poisson2.m" and make the following modifications.

- In addition to the current set of distances dr from each grid point to the point (diag(R)'/2), compute a new set of distances dr2 from each grid point to the point (diag(R)'/2+[x,0,0]).
- Because these Gaussian charges are to represent the two nuclei in the hydrogen molecule, be sure to *add* them together (not subtract) to form the total density n.
- Because we are interested only in the energy of interaction of the two Gaussians and not their self-energy, you should printout the value of Unum-Uself where Uself$\equiv 1/(2\sqrt{\pi})(1/\sigma_1 + 1/\sigma_2)$.
- You may remove any plotting and analytic tests of phi.

Debugging: You should find that at a separation of x=4.00 and widths sigma1=sigma2=0.5 you get results which are the same to within about 0.025 millihartree for setup parameters S=[32; 32; 32] and R=diag([16; 16; 16]) as you do for setup parameters S=[64; 64; 64] and R=diag([16; 16; 16]). (Be sure to modify *and rerun* "setup.m" to change these parameters and to make sure that the changes take effect!) More importantly, your result should change by only about 1 millihartree when you change to sigma1=sigma2=0.25 and evaluate at S=[64; 64; 64], R=diag([16; 16; 16]). All of these results should be about -0.094 hartree.

Finally, using the last of the above sets of parameters, (sigma1=sigma2=0.25, S=[64;64;64], R=diag([16; 16; 16])), calculate and save in a file for later use the values of Unum-Uself for nuclei at separations x=0.50, 1.00, 1.25, 1.50, 1.75, 2.00, 4.00 and 6.00 bohr.

1.2 Electron-nuclear potential (-Z/r)

Previously, you solved the Kohn-Sham equations in the very simple potential coming from a simple harmonic oscillator. For most electronic structure calculations, however, the potential comes from the interaction

between electrons and nuclei with the form

$$V(\vec{r}) = -\sum_I \frac{Z_I}{|\vec{r} - \vec{r}_I|}, \tag{1}$$

where Z_I and $\vec{r}_I$ are the charge and location of each nucleus.

Our approach to funding the potential Vdual from the nuclei for our periodic calculations is based on our standard approach to solving Poisson's equation,

```
phinuc=cI(Linv((-4*pi)*O(cJ(rhonuc))));
```

and our the definition of Vdual from Problem Set #8,

```
Vdual=cJdag(O(cJ(-phinuc)));
```

where the extra '-' in front of phinuc corresponds to the minus sign in Eq. (1). Combining the above two results gives

```
Vdual=cJdag(O(Linv((4*pi)*O(cJ(rhonuc)))));
```

where we have used the fact that $\mathcal{J}(\mathcal{I}(\vec{v})) = \vec{v}$.

The only difficulty with this approach is that rhonuc represents a point charge, whose density is zero everywhere but at a single point where the density is infinite. We can, however, find the expansion coefficients $[\text{cJ(rhonuc)}]_{\vec{G}} \equiv \hat{\rho}_{\vec{G}}$ mathematically. To do this, we note that

$$\rho(\vec{r}) \equiv \sum_{\vec{G}} \hat{\rho}_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

so that

$$\begin{aligned} \int e^{-i\vec{G}\cdot\vec{r}} \rho(\vec{r})\, dV &= \int e^{-i\vec{G}\cdot\vec{r}} \sum_{\vec{G}'} \hat{\rho}_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}}\, dV \\ &= \det(\mathbf{R})\, \hat{\rho}_{\vec{G}}, \end{aligned}$$

where $\det(\mathbf{R})$ is the volume of the cell. Therefore,

$$\hat{\rho}_{\vec{G}} = \frac{1}{\det(\mathbf{R})} \int e^{-i\vec{G}\cdot\vec{r}} \rho(\vec{r})\, dV.$$

In the case of a single nucleus, $\rho(\vec{r})$ is a point charge centered at location $\vec{r}_I$ with total integral Z_I. Thus, we have

$$\hat{\rho}_{\vec{G}} = \frac{Z_I}{\det(\mathbf{R})} e^{-i\vec{G}\cdot\vec{r}_I}.$$

In octave notation, the above expression becomes

```
rhohat=ZI/det(R)*exp(-i*G*rI);
```

where ZI is the charge of the nucleus and rI is a column vector containing its location. Finally, for the case of multiple nuclei, one should sum a series of such contributions, one for each nucleus.

1.2.1 Debugging

As a test, perform a three-dimensional calculation of a hydrogen atom as follows.

First, compute the potential energy of the periodic array of nuclei, proceeding as you did in Problem 1.1 with parameters sigma=0.25, S=[64;64;64], R=diag([16; 16; 16])), but placing just a single nucleus at the center of the cell. Be sure to subtract the self-energy, $1/(2\sqrt{\pi}\sigma)$.

Then, make a copy of "dft.m" called "Hatom.m" and replace the evaluation of Vdual there with the above octave expressions for rhohat (which represents J(rhonuc)) and Vdual for a Hydrogen nucleus (charge ZI=1) located at the center of the cell (rI=[8;8;8]) and run "Hatom.m" for a single state with one electron (gbl_f=1, Ns=1) with S=[64;64;64], R=diag([16; 16; 16]).

When your code functions properly (and you add the nuclear-nuclear potential energy), you should find a result within 1 millihartree of what you get either from your atomic code (with the VWN form for ϵ_{xc}) or from looking directly on the NIST web site result. Now, though, you are doing a full three-dimensional calculation, without artificially imposing any spherical symmetry!

1.3 Hydrogen molecule

Finally, make a copy of your file "Hatom.m" called "H2.m". In "H2.m", set rhohat equal to the sum of the expansion coefficients for two densities, that from the hydrogen potential you calculated above for a hydrogen nucleus at rI=[8;8;8] and a second just like it but centered at rI=[8;8;8]+[1.5;0;0]. Be sure also to include the fact that the H_2 molecule has two electrons.

You should find a total energy (when you add the nuclear-nuclear part from Problem 1.1) of -1.136 hartree. Subtracting from this twice the energy you found for the isolated atom then gives your prediction for the energy relative to the two atoms being isolated at infinite separation from each other. Your result for this "bonding energy" should be negative, indicating that the atoms prefer to be together rather than isolated.

Using this approach, compute the total "bonding energy" of the hydrogen molecule for the separations 0.50, 1.00, 1.25, 1.50, 1.75, 2.00, 4.00 and 6.00 bohr. Make a plot of your results. From the plot, determine the bond-length of H_2 and compare with the experimental result from a standard reference such as the CRC handbook. Show the plot to the grader to get credit for this problem!