

Homework5

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1 DFT calculation of an ammonia molecule

Based on the data from the website and some articles, I set the N-H bond length of the ammonia is $1.01\text{\AA} = 1.91\text{bohr}$ and the angle between the bond is 107° . So the coordinate of the atoms can be written as:

$$\begin{aligned} N &: 0.0 \quad 0.0 \quad 0.0 \\ H1 &: 1.773 \quad 0.0 \quad -0.71 \\ H2 &: -0.887 \quad 1.535 \quad -0.71 \\ H3 &: -0.887 \quad -1.535 \quad -0.71 \end{aligned}$$

1.1 Computation of the electronic ground state energy

1.1.1 Parameters meaning

cell: The variable cell is the unit cell parameters, containing the coordinates of the three lattice vectors defining the unit cell.

atom: The command atom could add an atom to the current sample.

ecut: The variable ecut is the plane wave basis energy cutoff.

PSDA: PSDA is one of the choice algorithm of the variable wf_dyn(wave function dynamics control variable). Preconditioned Steepest Descent with Anderson acceleration. Wave functions are updated as with the PSD option, and convergence is accelerated by the Anderson scheme (D. G. Anderson, JACM 12, No 4, pp. 547-560 (1965)).

ecutprec: A variable which preconditioning energy cutoff. The ecutprec variable defines the energy cutoff used in the preconditioner for electronic structure optimization. Corrections to the electronic wave functions are preconditioned in Fourier space using a diagonal preconditioning matrix K whose elements are defined by

$$k(G) = \begin{cases} \frac{1}{2E_{\text{cut}}^{\text{prec}}} & \frac{1}{2}G^2 < E_{\text{cut}}^{\text{prec}} \\ \frac{1}{G^2} & \frac{1}{2}G^2 \geq E_{\text{cut}}^{\text{prec}} \end{cases} \quad (1)$$

The value of ecutprec must be given in Rydberg units. Preconditioning is only used if the wf_dyn variable is set to either PSD, PSDA or JD. If ecutprec = 0, an automatic preconditioner is used. The default value of ecutprec is zero (automatic preconditioning). Should be non-negative real numbers smaller than or equal to ecut.

scf_tol: A variable scf_tol is the tolerance for convergence of SCF iterations. The scf_tol variable determines the energy tolerance criterion for convergence of SCF iterations.

randomize_wf: A command adding a random perturbation to electronic wave functions. The scf_tol variable determines the energy tolerance criterion for convergence of SCF iterations.

run: A command updating electronic wave functions and/or atomic position and/or unit cell. The run command starts a simulation in which atomic positions, electronic wave functions, and/or unit cell are updated.

LDA: LDA is a choice of the variable xc. LDA: Local Density Approximation, Ceperley-Alder data. This is the default. A class of approximations to the exchange–correlation (XC) energy functional in density functional theory (DFT) that depend solely upon the value of the electronic density at each point in space (and not, for example, derivatives of the density or the Kohn–Sham orbitals).

1.1.2 Total energy and ecut

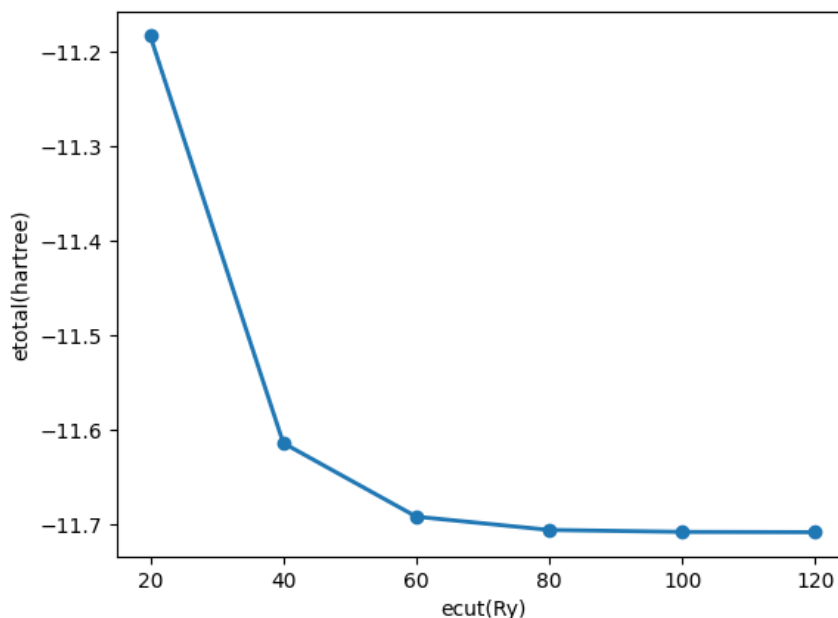


Figure 1: converged total energy as a function of ecut

1 shows the converged total energy going with the ecut. The total energy does decrease with increasing ecut. Because the wave function plane wave basis consists of all plane waves having a kinetic energy smaller than ecut. If the ecut is small, the number of wave vectors you use to calculate the energy will be small. In this way, the situation you calculate is further away than the ground state. Then the energy will be higher than the energy of which the ecut is larger.

1.2 Geometry optimization

We cannot run a CG minimization before determining the ground state of the electrons for one fixed, starting configuration. One thing is that some methods calculating the ground state of electrons are SCF, if you start the minimization before the wavefunction going self-consistence, the ground state you get of the electrons will be wrong then will also harm the geometry optimization. The other thing is that if you do the geometry optimization based on a incorrect electron state the optimization will also going wrong.

After the geometry optimization the position of the atoms are listed:

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N : -0.00065542   - 0.00000367   0.00019521
H1 : 1.79831215   0.00000187   - 0.70757661
H2 : -0.89867704   1.55709841   - 0.71069222
H3 : -0.89868485   - 1.55710007   - 0.71068575

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The total energy after the optimization is -11.70731169 hartree. I calculated the bond length and the bond angle based on the positions I got from the geometry optimization. We can get the bond

length should be 1.933bohr , 1.933bohr and 1.933bohr while the bond angles should be 107.32° , 107.33° and 107.32° . You can see that this result is very similar to the initial length and angles we set which we got from the experiments. The structure's symmetry point group is C_{3v} .

1.3 Frozen phonons

1.3.1 Using optimized structure to do the SCF calculation

Used the optimized structure to do the SCF calculation. The result I got is list:

$$\begin{aligned} N &: -0.00057150 & -0.00000450 & 0.00017417 \\ H1 &: 1.79815132 & -0.00000009 & -0.70799784 \\ H2 &: -0.89883502 & 1.55713741 & -0.71050242 \\ H3 &: -0.89884286 & -1.55714305 & -0.71049887 \end{aligned}$$

I also calculated the bond length are all 1.933bohr and the bond angle are all about 107.3° . We can see both atomic and electronic structures are converged very well because the progress must be a iterative convergence process. After the electronic structure is converged then we calculate the atomic structure based on it after that we compute the electronic structure again based on the new atomic structure. Things will going like that until we get a result both electronic and atomic structure are converged.

1.3.2 Displacing atoms and compute total energies

I displaced the atoms and recorded the total energies and the forces per the displacement.

1.3.3 Computing second derivatives of total energies with respect to ionic positions and the dynamical matrix

Using the result we get from the process before. We can set that:

$$D_{I\alpha;J\beta} = -\frac{1}{\sqrt{M_I M_J}} \frac{\partial F_{I\alpha}}{\partial R_{J\beta}} = -\frac{1}{\sqrt{M_I M_J}} \frac{F_{I\alpha}(R_{J\beta} + \Delta) - F_{I\alpha}(R_{J\beta} - \Delta)}{2\Delta} \quad (2)$$

where I and J are the indexes of the atoms and the α and β are the indexes of the orientation. We have 4 atoms and 3 dimensions so the dynamical matrix should be a 12×12 matrix.

$$\begin{bmatrix} 4.38 \times 10^{-2} & 1.36 \times 10^{-7} & -3.85 \times 10^{-5} & -9.52 \times 10^{-2} & -1.87 \times 10^{-7} & 4.32 \times 10^{-2} & -3.43 \times 10^{-2} & 3.49 \times 10^{-2} & -2.16 \times 10^{-2} & -3.43 \times 10^{-2} & -3.49 \times 10^{-2} & -2.16 \times 10^{-2} \\ -2.05 \times 10^{-6} & 4.38 \times 10^{-2} & -1.14 \times 10^{-6} & -1.54 \times 10^{-5} & -1.42 \times 10^{-2} & 1.07 \times 10^{-5} & 3.51 \times 10^{-2} & -7.48 \times 10^{-2} & 3.75 \times 10^{-2} & -3.51 \times 10^{-2} & -7.48 \times 10^{-2} & -3.75 \times 10^{-2} \\ 2.93 \times 10^{-5} & -4.16 \times 10^{-6} & 1.33 \times 10^{-2} & 2.97 \times 10^{-2} & 4.97 \times 10^{-6} & -1.66 \times 10^{-2} & -1.49 \times 10^{-2} & 2.58 \times 10^{-2} & -1.67 \times 10^{-2} & -1.49 \times 10^{-2} & -2.58 \times 10^{-2} & -1.67 \times 10^{-2} \\ -9.53 \times 10^{-2} & -1.87 \times 10^{-7} & 3.00 \times 10^{-2} & 3.86 \times 10^{-1} & 5.00 \times 10^{-7} & -1.31 \times 10^{-1} & -1.49 \times 10^{-2} & -3.50 \times 10^{-3} & 9.59 \times 10^{-3} & -1.49 \times 10^{-2} & 3.50 \times 10^{-3} & 9.59 \times 10^{-3} \\ -2.91 \times 10^{-5} & -1.42 \times 10^{-2} & 1.37 \times 10^{-5} & 8.79 \times 10^{-5} & 5.25 \times 10^{-2} & -1.96 \times 10^{-5} & 2.99 \times 10^{-2} & 2.99 \times 10^{-4} & -1.21 \times 10^{-2} & -2.98 \times 10^{-2} & 3.83 \times 10^{-4} & 1.21 \times 10^{-2} \\ 4.30 \times 10^{-2} & 4.97 \times 10^{-6} & -1.66 \times 10^{-2} & -1.30 \times 10^{-1} & 4.03 \times 10^{-5} & 6.28 \times 10^{-2} & -1.54 \times 10^{-2} & 2.29 \times 10^{-3} & -4.58 \times 10^{-4} & -1.53 \times 10^{-2} & -2.32 \times 10^{-3} & -4.30 \times 10^{-4} \\ -3.41 \times 10^{-2} & 3.52 \times 10^{-2} & -1.49 \times 10^{-2} & -1.55 \times 10^{-2} & 2.96 \times 10^{-2} & -1.50 \times 10^{-2} & 1.35 \times 10^{-1} & -1.44 \times 10^{-1} & 6.48 \times 10^{-2} & 8.02 \times 10^{-3} & -1.69 \times 10^{-2} & 5.68 \times 10^{-3} \\ 3.51 \times 10^{-2} & -7.48 \times 10^{-2} & 2.59 \times 10^{-2} & -3.25 \times 10^{-3} & 1.75 \times 10^{-4} & 2.39 \times 10^{-3} & -1.45 \times 10^{-1} & 3.02 \times 10^{-1} & -1.14 \times 10^{-1} & 1.69 \times 10^{-2} & -2.25 \times 10^{-2} & 1.44 \times 10^{-2} \\ -2.15 \times 10^{-2} & 3.74 \times 10^{-2} & -1.68 \times 10^{-2} & 1.00 \times 10^{-2} & -1.25 \times 10^{-2} & -2.17 \times 10^{-4} & 6.48 \times 10^{-2} & -1.13 \times 10^{-1} & 6.34 \times 10^{-2} & 5.63 \times 10^{-3} & -1.44 \times 10^{-2} & -6.32 \times 10^{-4} \\ -3.41 \times 10^{-2} & -3.52 \times 10^{-2} & -1.49 \times 10^{-2} & -1.54 \times 10^{-2} & -2.96 \times 10^{-2} & -1.50 \times 10^{-2} & 8.01 \times 10^{-3} & 1.69 \times 10^{-2} & 5.66 \times 10^{-3} & 1.35 \times 10^{-1} & 1.44 \times 10^{-1} & 6.48 \times 10^{-2} \\ -3.51 \times 10^{-2} & -7.48 \times 10^{-2} & -2.59 \times 10^{-2} & 3.36 \times 10^{-3} & 2.57 \times 10^{-4} & -2.46 \times 10^{-3} & -1.70 \times 10^{-2} & -2.25 \times 10^{-2} & -1.45 \times 10^{-2} & 1.45 \times 10^{-1} & 3.02 \times 10^{-1} & 1.14 \times 10^{-1} \\ -2.15 \times 10^{-2} & -3.74 \times 10^{-2} & -1.68 \times 10^{-2} & 1.01 \times 10^{-2} & 1.25 \times 10^{-2} & -2.73 \times 10^{-4} & 5.62 \times 10^{-3} & 1.45 \times 10^{-2} & -6.95 \times 10^{-4} & 6.48 \times 10^{-2} & 1.13 \times 10^{-1} & 6.34 \times 10^{-2} \end{bmatrix}$$

Figure 2: Initial dynamical matrix

Using code to compute the dynamical matrix, like 2. You can see that it is not a symmetric matrix but you can see some symmetric elements here, like the line 12 and the column 12. Things like that the indexes of the element closer to (12,12), the symmetry is easier to see.

Cause of that matrix is not symmetric, I need to symmetrize it, just use:

$$D' = \frac{1}{2}(D + D^T) \quad (3)$$

Then I get a symmetric matrix. After that I used codes to get the eigenvalues of the matrix, as:

$$\begin{bmatrix} 4.3655 \times 10^{-1} \\ 4.7269 \times 10^{-1} \\ 4.7288 \times 10^{-1} \\ 9.3789 \times 10^{-2} \\ 9.4465 \times 10^{-2} \\ 3.4039 \times 10^{-2} \\ -5.2679 \times 10^{-4} \\ 5.1979 \times 10^{-4} \\ -1.751 \times 10^{-4} \\ 4.5621 \times 10^{-5} \\ -3.9949 \times 10^{-5} \\ -9.0007 \times 10^{-6} \end{bmatrix}$$

we can see that the first 6 eigenvalues are much larger than the rest, so I assume that the last 6 approx to 0. Then I only get 6 eigenvalues and they are all positive.

Based on the definition, the 6 eigenvalues and their eigenvectors show the vibration frequency and the vibration modes corresponding. The eigenvalues are then square of the characteristic angular frequency in a reduced unit system. The unit should be:

$$\frac{\text{hartree}}{\text{bohr}^2 * \text{atomunit}} \approx 9.39 \times 10^{29} s^{-2} \quad (4)$$

Using the unit transition we can get the 6 characteristic frequency in cm^{-1} :

$$\begin{bmatrix} 3400.73 \\ 3538.66 \\ 3539.39 \\ 1576.27 \\ 1581.93 \\ 949.59 \end{bmatrix}$$

And the eigenvector can indicate the vibration model of the atom corresponding to the eigenvalue.

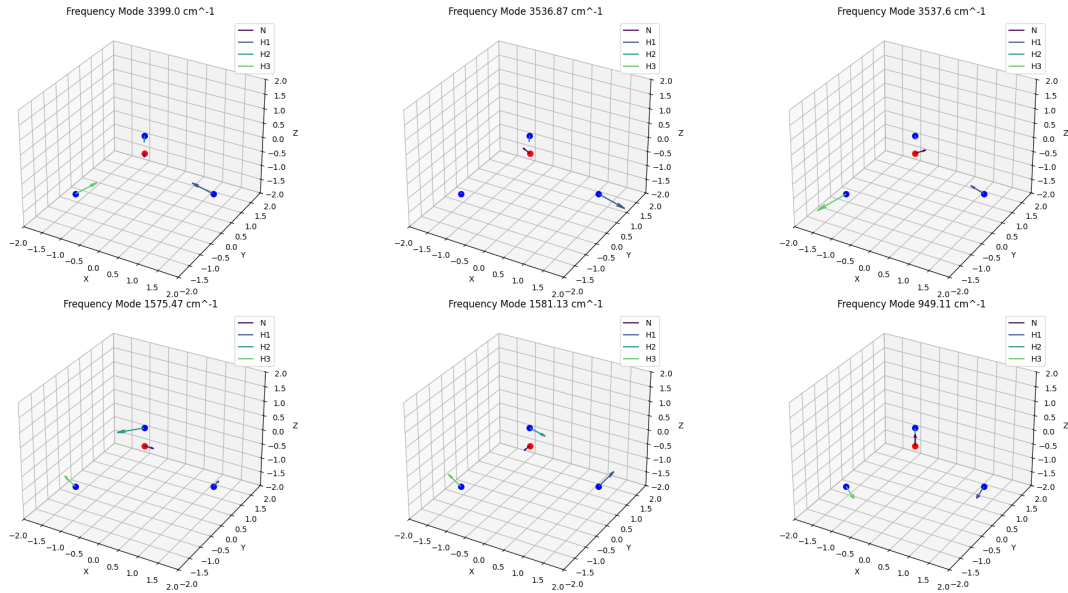


Figure 3: eigenvectors

The first picture shows three hydrogen atoms vibrating in the same phase along the bonding direction. The second figure shows that one of the H atom is like stopping and other atoms' vibration

orientation is in a plane. The third picture shows two hydrogen atoms and one nitrogen atom vibrating in the same phase along the bonding direction, and the other hydrogen atom vibrating in opposite phases. The fourth picture shows two hydrogen atoms vibrating in the same plane, with a hydrogen atom and an N atom vibrating in another plane. The fifth picture shows the atoms vibrating approximately in the same plane, with a hydrogen atom and an N atom vibrating in opposite directions in one direction. The sixth image shows the atoms oscillating perpendicular to the bonding direction. You can run my code to see the details.

As a summary, the 1st first shows symmetric stretching vibration (symmetric stretching of N-H bonds), the second and third figures show asymmetric stretching vibration (stretching of N-H bonds outside the plane of symmetry). The fourth and fifth figures show the shear vibration (H-N-H angular motion). The last figure shows the tilt vibration (movement of nitrogen atoms along the axis of symmetry).

1.3.4 Comparing the results with measured vibrational frequencies

I found some experimental results and the analysis in some articles. [1] shows the results from high-resolution infrared spectra of a number of fundamental, overtone, and combination bands. [2] shows a summary of the results from other experiments[3] and analyses some vibration mode based on the symmetry[2][3]. For every results I got I could find a result from the experiment which is similar to it as list:

<i>results</i>	<i>experiment</i>
3400.73	3336.21[2][3]
3538.66	3444[2]
3539.39	3444[2]
1576.27	1627[2]
1581.93	1627[2]
949.59	950[2]

As [3], in theory there are only 4 modes of vibration, and it is also can fit my results. Details can be get from the point group theory.

1.4 HOMO and LUMO

I used VMD to visualize the electronic orbitals, noted that the gray color means the negative wavefunction while the red color respect for the positive wavefunction. The HOMO orbital is in 4 and the LUMO orbital is 5. Maybe you can see that the position of the positive and negative wavefunctions are inverse but I think taking about it is boring. My results are similar to the figures in [lecture notes for NH3](#).

You can also find some results in the articles[4]. Then we go to the symmetry part, it can be seen that the electron cloud is symmetrical along the bonding direction. The symmetry contains a 3m(3-fold and mirror symmetry) symmetry So they are both A_1 (or whole C_{3v}) symmetry of the C_{3v} point group.

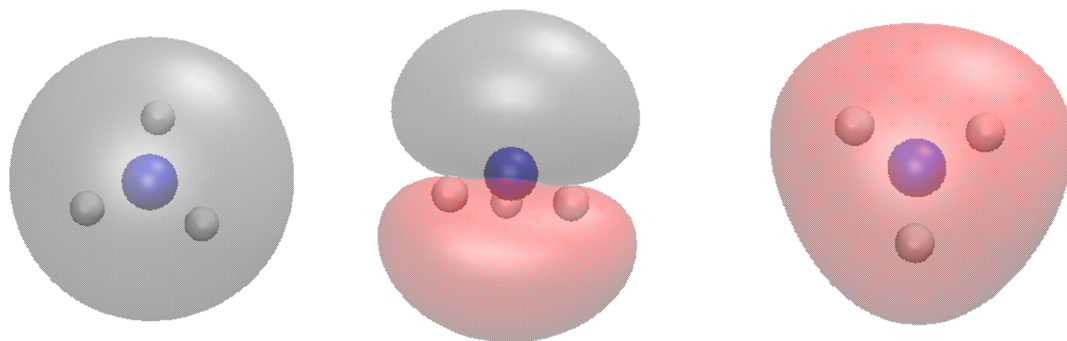


Figure 4: Some figures of the HOMO orbitals. The value of the surface of the positive wavefunction is +1.0, and for Negative is -1.0.

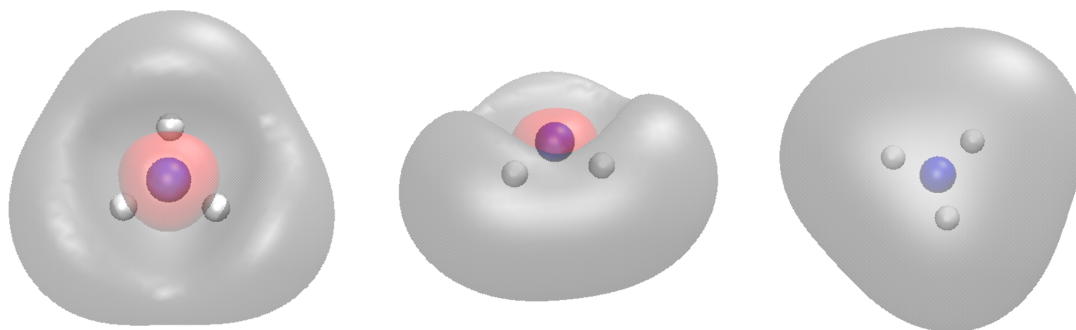


Figure 5: Some figures of the LUMO orbitals. The value of the surface of the positive wavefunction is +0.5, and for Negative is -1.5

References

- [1] W. S. Benedict and Earle K. Plyler. Vibration-rotation bands of ammonia: II. the molecular dimensions and harmonic frequencies of ammonia and deuterated ammonia. *Canadian Journal of Physics*, 35(10):1235–1241, 1957.
- [2] JM Price, MW Crofton, and Yuan T Lee. Vibrational spectroscopy of the ammoniated ammonium ions $\text{NH}_4^+ (\text{NH}_3)_n$ ($n = 1-10$). *The Journal of Physical Chemistry*, 95(6):2182–2195, 1991.
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- [4] Eva Zurek, Peter P. Edwards, and Roald Hoffmann. A molecular perspective on lithium-ammonia solutions. *Angewandte Chemie International Edition*, 48(44):8198–8232, 2009.