

Report for the density-functional perturbation theory

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ABINIT is a software suite to calculate the optical, mechanical, vibrational, and other observable properties of materials based on the density function theory (DFT). In this report, we use the density-functional perturbation theory (DFPT) to calculate a second derivative of the total energy. As a comparison, we also apply the frozen-phonon approach to calculate this amount, and show the consistency of the result. Moreover, we apply DFPT to calculate the phonon frequencies and eigenvectors at Γ point, and other q -point in the Brillouin Zone.

I. THEORY AND ALGORITHM

In the traditional DFT theory, one solve the following self-consistent Kohn-Sham equation,

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}\right) \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}), \quad (1)$$

where V_{SCF} is the self-consistent field containing the external potential, the electron potential and the exchange-correlation potential. The ground state charge density distribution is given in terms of the auxiliary Kohn-Sham orbitals, $\psi_n(\mathbf{r})$,

$$n(\mathbf{r}) = 2 \sum_{n=1}^{N/2} |\psi_n(\mathbf{r})|^2, \quad (2)$$

where N is the number of electrons, and the system is supposed to be non-magnetic.

The electron-density linear response of a system determines the matrix of its interatomic force constants. To conduct the perturbation calculation, we first linearize the wave function, density and potential variation. Linearization of (2) leads to

$$\Delta n(\mathbf{r}) = 4 \operatorname{Re} \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \Delta \psi_n(\mathbf{r}), \quad (3)$$

where the finite difference operator Δ^λ is defined as

$$\Delta^\lambda F = \sum_i \frac{\partial F_\lambda}{\partial \lambda_i} \Delta \lambda_i. \quad (4)$$

Since the external potential (both unperturbed and perturbed) is real, each Kohn-Sham eigenfunction and its complex conjugate are degenerate. As a consequence, the imaginary part of the sum vanishes, so that the prescription to keep only the real part can be dropped.

The variation of Kohn-Sham orbitals $\Delta_n(\mathbf{r})$ is obtained by standard first-order perturbation theory,

$$(H_{SCF} - \epsilon_n) |\Delta \psi_n\rangle = -(\Delta V_{SCF} - \Delta \epsilon_n) |\psi_n\rangle, \quad (5)$$

where

$$H_{SCF} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}(\mathbf{r}) \quad (6)$$

is the unperturbed Kohn-Sham Hamiltonian.

$$\Delta V_{SCF} = \Delta V(\mathbf{r}) + e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left. \frac{dv_{xc}(n)}{dn} \right|_{n=n(\mathbf{r})} \Delta n(\mathbf{r}) \quad (7)$$

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is the first order correction to the self-consistent potential, and $\Delta\epsilon_n = \langle \psi_n | \Delta V_{SCF} | \psi_n \rangle$ is the first order variation of the Kohn-Sham eigenvalue ϵ_n .

The equations shown above form a set of self-consistent equations for the perturbed system completely analogous to the Kohn-Sham equations in the unperturbed case. The first-order correction to a given eigenfunction of the Schrodinger equation is often expressed in terms of a sum over the spectrum of the unperturbed Hamiltonian

$$\Delta\psi_n(\mathbf{r}) = \sum_{m \neq n} \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{SCF} | \psi_n \rangle}{\epsilon_n - \epsilon_m} \quad (8)$$

running over all the states of the system, occupied and empty, with the exception of the state being considered, for which the energy denominator would vanish. Therefore, the linearization of electron-density is

$$\Delta n(\mathbf{r}) = 4 \sum_{n=1}^{N/2} \sum_{m \neq n} \psi_n^*(\mathbf{r}) \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{SCF} | \psi_n \rangle}{\epsilon_n - \epsilon_m}, \quad (9)$$

which shows that the contributions to the electron-density response coming from products of occupied states cancel each other, so that the m index can be thought of as attaching to conduction states only. This is equivalent to saying that the electron-density distribution does not respond to a perturbation, which acts only on the occupied-state manifold.

One of the greatest advantages of DFPT, as compared to other non-perturbative methods for calculating the vibrational properties of crystallines solids (such as the frozen-phonon or molecular-dynamics spectral analysis methods), is that within DFPT the response to perturbations of different wavelengths are decoupling, enabling people to calculate phonon frequencies at arbitrary wave vectors \mathbf{q} avoiding the use of supercells and with a workload that is essentially independent of the phonon wavelength. This property will be used in this report.

We calculate the force constants in this report, which is a second derivative of the total energy,

$$\frac{\partial^2 E_{tot}}{\partial R_I^\alpha \partial R_J^\alpha} = -\frac{\partial F_J^\beta}{\partial R_I^\alpha}. \quad (10)$$

with two different approaches, i.e., frozen-phonon method and DFPT.

II. NUMERICAL CALCULATION

In the first part, we calculate a second derivative of the total energy with frozen-phonon approach. In this method, we just simply compare the total energy of unperturbed lattice and the lattice with a given perturbation. The derivative can be calculated by finite difference method. As an example, we use AlAs as the test-bench for the numerical method. AlAs is in a cubic β -ZnS structure, where every lattice point is composed of one Al and one As atom, and the lattice points form a face-centered lattice. The structure of AsAl is similar to the structure of diamond, but the every lattice point has two different type of atoms.

First, we perform the traditional DFT calculation to obtain the ground state geometry of AlAs. In this run, the computation shows that the total energy is -9.7626837450E+00 Ha, which will be the start point of frozen-phonon method. Then, we perturb the reduced coordinate of Al atom along the first axis, and we can make an estimate of the second derivative of the total energy with respect to the reduced coordinate thanks to finite-difference formulas. Technically, we set the reduced coordinate of Al as $\mathbf{xred} = (0.001, 0.0, 0.0)$ to perform the DFT calculation. In such run, the total energy of perturbed lattice is -9.76268124105767E+00 Ha. For the following run, we will perform the computation based on the ground state wavefunction calculated in this unperturbed run.

We can estimate the second derivative directly from the energy difference. Note that the total energy is symmetric with respect to the perturbation, so that it has no linear term. The difference between the unperturbed and perturbed system is thus one half of the square of the coordinate change (0.001) times the second derivative of total energy. Therefore, we can estimate the second derivative as 5.0078902589 Ha.

Alternatively, we can start from the reduced gradients. The value of the reduced gradient with respect to a displacement of the Al atom along the first reduced axis is 0.005007937776 Ha. At first order, this quantity is the product of the second derivative by the reduced coordinate difference. The estimate of the second derivative is thus 5.007937776 Ha. The agreement with the other estimate is rather good.

Further more, one can set the perturbation parameter from 0.001 to 0.002 to have a better estimation. The doubling of the perturbation allows for a simple higher-order estimation. The similar procedure as above leads to the second derivative as 5.00800219 Ha from finite difference of energy and 5.008153784 Ha from finite difference of forces.

Thus, we conclude that the perturbation parameter in current order of magnitude is adequate to obtain a satisfying estimation of the second derivative.

Then, we use the DFPT method to re-calculate the same quantity. We set the related parameters **rfphon**, **rfatpol**, **rfdir**, **nqpt** and **qpt** to set the detailed perturbation atom, type and corresponding wavevectors. After several iterations, the second derivative converge at the value 5.0078557427888 Ha, which is in a good agreement with former result.

After testing the performance of DFPT, we start to calculate quantities more interesting. As an example, we calculate the dynamical matrix at Γ point. We change the input parameter **rfatpol** and **rfdir**, and all the atoms will be displaced in all the directions. Then we obtain the dynamical matrix and then diagonalize it to calculate the phonon frequencies as follows

Phonon frequencies calculation

Phonon wavevector (reduced coordinates) :	0.00000	0.00000	0.00000		
Phonon energies in Hartree :					
	2.558879E-06	2.558879E-06	2.558880E-06	1.568559E-03	1.568559E-03
	1.568559E-03				
Phonon frequencies in cm ⁻¹ :					
-	5.616090E-01	5.616091E-01	5.616093E-01	3.442590E+02	3.442590E+02
-	3.442590E+02				

In the computation, only the response to two perturbations were computed explicitly, while the other four can be deduced from the two by using the symmetries of the lattice. In another word, there are two different irreducible perturbations for the AlAs lattice, therefore, there are only two distinct value for the phonon frequencies.

At last, we can compute the phonon frequencies at non-zero q by setting different computation parameters mentioned above, especially **qpt**. We conduct the calculation in the same process, i.e., first calculate the ground state wavefunctions, and finish the phonon calculation starting from the ground state wavefunctions. The result of phonon frequencies at other q points also show great consistency with former literature.

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