Calculation on Polarization and Finite electric fields with ABINIT

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With the development of theory of Berry phase, research on polarization using topological paradigm has attracted increasing interests recently. The fundamental theory of polarization under Berry phase perspective was proposed and then developed by R.D.King-Smith[1] and D.Vanderbilt[2]. In the first part of this report, we briefly introduced the basic therry. Then we followed their work and utilized ABINIT to calculate the Berry phase in AlAs under zero field and concluded that polarization from Berry phase analysis was in excellent agreement with DFPT. Next, we calculated the Berray phase in AlAs under finite field from which we deduced the Born effective charge and electric susceptibility. The results were consistent with DFPT method with acceptable deviation.

I. BASIC THEORY OF BERRY PHASE AND POLARIZATION

Berry phase was first introduced by Sir Michael Victor Berry in 1984 which depicts the geometry phase the system obtains after a cyclic adiabatic process. The general form of non-degenerate Berry phase is

$$\gamma_n = i \oint_C \langle n, t | \nabla_{\mathbf{R}} | n, t \rangle \, d\mathbf{R} \tag{1}$$

where \boldsymbol{R} is an arbitrary time-dependent variable of the Hamiltonian in the adiabatic evolution. Among all the time-dependent variables and adiabetic loops, wave vector of quasi-momentum and the boundary of first Brillouin zone is of great interest since it is connected with band structure and polarization of material. The phase is defined as

$$\gamma_n = i \oint_{BZ} \langle n, t | \nabla_{\boldsymbol{k}} | n, t \rangle \, d\boldsymbol{k} \tag{2}$$

which is called Zak phase. Here, k represents quasimomentum while BZ denotes the first Brillouin zone. In order to straddle the gap between Berry phase and polarization, we first write the fomular of drift velocity.[3]

$$v_n(q) = \frac{\partial \epsilon_n(q)}{\hbar \partial q} - i \left[\left\langle \frac{\partial u_n}{\partial q} \middle| \frac{\partial u_n}{\partial t} \right\rangle - \left\langle \frac{\partial u_n}{\partial t} \middle| \frac{\partial u_n}{\partial q} \right\rangle \right] \quad (3)$$

The first term is the common drift velocity when Hamiltonian is time independent while the second is exactly the Berry curvature. As a consequence, a net current can be generated. Since the integral of $\frac{\partial \epsilon_n(q)}{\hbar \partial q}$ over BZ equals zero, the current is in the form

$$\boldsymbol{j} = e \sum_{n} \int_{BZ} \frac{dq}{2\pi} \Omega_{qt}^{n} \tag{4}$$

Thus, we have deduced the current created by adiabatic evolution of bands, which is equivalent to the integral on Berry curvature over BZ[3].

On the other hand, with Gauss's law and equation of continuity , we have

$$\nabla \cdot \boldsymbol{P} = -\rho$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \boldsymbol{j} = 0$$
(5)

Thus, with equation (4), time derivative of polarization can be determined up to a field without source.

$$\nabla \cdot \left(\frac{\partial \boldsymbol{P}}{\partial t} - \boldsymbol{j}\right) = 0 \tag{6}$$

Change of polarization is

$$\Delta \boldsymbol{P} = e \sum_{n} \int dt \int_{BZ} \frac{dq}{2\pi} \Omega_{qt}^{n} \tag{7}$$

It can be seen that polarization is determined by Berry phase accumulated after an adiabetic process. In addition, by defining localized Wannier functions, we can understand equation (7) in a more direct and heuristic way.

Wannier function is defined as,

$$W_{\boldsymbol{R}_{I}}^{n}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{k} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_{I}} \psi_{\boldsymbol{k}}^{n}(\boldsymbol{r})$$
(8)

in which N is the number of primitive cells, \mathbf{R}_I is the center where the Wannier function localized and $\psi_{\mathbf{k}}^n(\mathbf{r})$ is Block wave function denoted as $\psi_{\mathbf{k}}^n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}^n(\mathbf{r})$. Moreover, Wannier functions constitute an othonormal basis set which is essential in lattice model and tight binding picture. With inverse Fourier transformation and apply equation (8) into (7), we can get

$$\Delta \boldsymbol{P} = -e \sum_{n} \sum_{I} \int d\boldsymbol{r} \boldsymbol{r} |W_{\boldsymbol{R}_{I}}^{n}((\boldsymbol{r}))|^{2}$$
(9)

It can be interpreted that the \boldsymbol{P} is the dipole momentum of Wannier charge density, which is consistent with classical picture of polarization. This connection between microscopic property of materials and topological phase demonstrates the fundamental role of Berry phase and topological structure. With equation (9), we can in principal calculate change of polarization and current. However, in practice, the summation over all bands is intractable and unnecessary. For fermionic system, bands near fermi energy is most interested thus in section II, calculation of polarization is restricted to finite occupied bands.

Morever, not only conductive electrons but also lattice contribute to polarization according to equation (10)

$$\boldsymbol{P} = \frac{1}{V} \left[-\sum_{I} Z_{I} \boldsymbol{R}_{I} + \int d\boldsymbol{r} \rho_{e}(\boldsymbol{r}) \right]$$
(10)

where the summation and integral is over the whole piece of material. Thus, in section II we include the influence of lattice displacement to achieve more precise analysis and it turns out lattice ions' contribution are $2 \sim 4$ orders higher than electrons.

II. NUMERICAL CALCULATION OF POLARIZATION IN ALAS

A. Berry phase calculation of polarization in zero field

In this part, we first calculate polarization of AlAs in zero field and analyze three different situations in which $\tau = 0$ (corresponding to optimized structure), $\tau = +0.01$ and $\tau = -0.01$ (corresponding to Al displaces from optimized location 0.01 Bohr right and left). In order to finish the Berry phase calculation, parameters berryopt and *rfdir* are needed. *Berryopt* specifies the use of Berry phase in calculation and *rfdir* defines the direction along which reponse functions are calculated. Here, with the assignment of *berryopt*=-1 and rfdir=(1,1,1), total polarization for reciprocal lattice and real space lattice is obtained. The results are shown in Figure 1, where Al atom is at optimized position in figure a and on the right(left) +0.01(-0.01) (a.u.) of the optimized position in figure b(c). From previous data, we notice that ionic polarization is 3 orders higher than the electron Berry phase and we can calculate the Born effective charge through equation (11),

$$Z^* = \Omega_0 \frac{\boldsymbol{P}(\tau = +0.01) - \boldsymbol{P}(\tau = -0.01)}{2\tau} = 2.06 \quad (11)$$

where Ω_0 is the volume of the primitive cell in atomic unit. Born effective charge depicts the extent to which a change of polarization can be generated by the atom displacement.

Moreover, we analyse the piezoelectric constant by equation (12),

$$d_{\alpha\beta} = \frac{\partial P_{\alpha}}{\partial \sigma_{\beta}} \tag{12}$$

where σ is the strain at the position. From the output file, strain at $\tau = +0.01$ and $\tau = -0.01$ are obtained and the proper piezoelectric constant equals $-0.6491(C/m^2)$. In order to confirm the result, we also

calculate the piezoelectric constant using DFPT method which gives $-0.6491(C/m^2)$ in clamped ion condition and $0.0430(C/m^2)$ in relaxed ion condition. It turns out that the Berry phase calculation is consistent with clamped ion DFPT while the discrepancy between relaxed ion and clamped ion can be explained that relaxed atoms can redistribute to minimize the total energy which in turn reduces the polarization.

B. Finite electric field calculations

In this part, polarization with finite electric field is calculated. Compared to zero field situation, finite field calculation is more sutble since the electric field breaks the discrete translation symmetry, resulting in the failure of band structure. Thus, we first calculate the Berry phase at zero field and then we take increment steps corresponding to various value of electric field and use wavefunction obtained from former step to make the system evolve adiabatically.

In the calculation, we choose the parameter set as E = 0, E = +0.0001, E = -0.0001 and the direction of electric field is along (111). From the output file(the results are shown in figure.2), we can deduce the Born effective charge from equation (13) by using the data of forces under different electric fields.

$$F_{A,i} = Z^*_{A,ii}E + \Omega_0 \frac{d\chi}{d\tau} E^2$$
(13)

We can see that opposite electric field forces have same magnitude (relative error 10^{-3}) with different sign which means the qudratic term is negligible. Therefore, we find that the Born effective charge is

$$Z_{Al}^* \frac{F_{Al}(E = +0.0001) - F_{Al}(E = -0.0001)}{2 \times 0.0002} = 2.06$$
(14)

which matches the result in zero field Berry phase calculation and clamped ion DFPT. In order to determine the coefficient $\frac{d\chi}{d\tau}$, we need to consider higher field that requires much denser k-grid to converge the calculation, which is covered in the tutorial on static Non-linear properties.

The output file also include the polarization data under electric field mentioned above(results shown in figure.3). For polarization under electric field, we have

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k \tag{15}$$

where $\chi_{ij}^{(1)}$ is the linear susceptibility tensor while $\chi_{ijk}^{(2)}$ is the quadratic susceptibility tensor. From figure.3 we find that the quadratic term is ignorable which is the case in force-electric field relation. Thus the linear optical dielectric susceptibility is extracted as

$$\chi_{11}^{(1)} = \frac{P_1(E = +0.0001) - P_1(E = -0.0001)}{2 \times 0.0001} = 0.56756$$
(16)

larization in cartesian coordi he sum of the electronic and i Electronic berry phase: Ionic: Total:	nates (C/m^2): onic Berry phase has been folded into [-1, 1]) 0.418138377E-02 0.418138377E-02 0.418138377E-02 -0.154800587E+01 -0.154800587E+01 -0.154800587E+01 -0.154382449E+01 -0.154382449E+01 -0.154382449E+01	
(a) $\tau = 0$		
arization in cartesian coordi ne sum of the electronic and i Electronic berry phase: Ionic: Total:	nates (C/m^2): onic Berry phase has been folded into [-1, 1]) 0.234598001E-02 0.418196820E-02 0.418196820E-02 -0.154212551E+01 -0.154800587E+01 -0.154800587E+01 -0.153977953E+01 -0.154382391E+01 -0.154382391E+01	
(b) $\tau = +0.01$		
larization in cartesian coordin he sum of the electronic and id Electronic berry phase: Ionic: Total:	nates (C/m ² 2): onic Berry phase has been folded into [-1, 1]) 0.601795583E-02 0.418196820E-02 0.418196820E-02 -0.155388624E+01 -0.154800587E+01 -0.154800587E+01 -0.154786828E+01 -0.154382391E+01 -0.154382391E+01	
(c) $\tau = -0.01$		
FIG. 1. Polarization under different $displacement(a.u.)$.		
rtesian forces (hartree/b 1 -0.0000000000000 2 -0.000000000000000	ohr) at end: -0.00000000000000000000000000000000000	
(a) $E = 0$		
rtesian forces (hartree/ 1 0.00020614763233 2 -0.00020614763233	bohr) at end: 0.00020614763233 0.00020614763233 -0.00020614763233 -0.00020614763233	
(b) $E = 1$	0.0001	

(b) E = +0.0001cartesian forces (hartree/bohr) at end: -0.00020651240300-0.00020651240300-0.000206512403000.00020651240300 0.00020651240300 0.00020651240300 (c) E = -0.0001

FIG. 2. Force under different electric fields.(a.u.)

As a consequence, the optical dielectric constant is

$$\epsilon_{11} = 1 + 4\pi \chi_{11}^{(1)} = 8.13 \tag{17}$$

On the contrary, result from DFPT is 9.20. This difference comes from the slow pace at which the finite field calculation converges thus there still exists much to improve for this Berry phase-based method.

III. CONCLUSIONS

In this report, we followed the Ffield tutorial file and calculated the polarization under sero field and finite field by utilizing Berry phase method. First, we conducted zero field calculation and compared them with the result produced by DFPT method. It turned out Berry phase method was consistent with clamped ion regime while relaxed ion regime counteracted the polarization. Then we expanded our analysis to finite field. Since finite electric field break the discrete translation symmetry, we adiabatically manipulated the wave function under zero field to finite field and calculated the polarization, Born effetive charge, piezoelectric constant and dielectric susceptibility. In this situation, small gap between two method occurred. According to tutorial file, denser k-grid was necessery for finite field calcultion convergence and the stride also influenced the accuracy of former method. Therefore, there exists much subtleties to be explored.

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^[1] RD King-Smith and David Vanderbilt. Theory of polarization of crystalline solids. Physical Review B, 47(3):1651,

Polarization in cartesian coordinates (a.u.):		
(the sum of the electronic and	ionic Berry phase has been folded into [-1, 1])	
Electronic berry phase:	0.730822547E-04 $0.730822547E-04$ $0.730822547E-04$	
Total:	$-0.270500574E^{-01}$ $-0.270500574E^{-01}$ $-0.270500574E^{-01}$	
iotai.	0.2000201020 01 0.2000201020 01 0.2000201020 01	
(a) $E = 0$		
Polarization in cartesian coord (the sum of the electronic and Electronic berry phase: Ionic: Total:	<pre>inates (a. u.): ionic Berry phase has been folded into [-1, 1]) 0.129869847E-03 0.129869847E-03 0.129869847E-03 -0.270560574E-01 -0.270560574E-01 -0.270560574E-01 -0.269261876E-01 -0.269261876E-01 -0.269261876E-01</pre>	
(b) $E = +0.0001$		
Polarization in cartesian coordinates (a.u.): (the sum of the electronic and ionic Berry phase has been folded into [-1, 1]) Electronic berry phase: 0.163575020E-04 0.163575021E-04 0.163575022E-04 Ionic: -0.270560574E-01 -0.270560574E-01 -0.270396999E-01 Total: -0.270396999E-01 -0.270396999E-01 -0.270396999E-01		
(c) $E = -0.0001$		

FIG. 3. Polarization under different electric fields (a.u.).

[2] David Vanderbilt and RD King-Smith. Electric polarization as a bulk quantity and its relation to surface charge. *Physical Review B*, 48(7):4442, 1993. 82(3):1959, 2010.

[3] Di Xiao, Ming-Che Chang, and Qian Niu. Berry phase effects on electronic properties. *Reviews of modern physics*,