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Dielectric Tensor, Effective Charges, and Phonons in α-Quartz by Variational Density-Functional Perturbation Theory

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A new method is introduced to calculate response functions within density-functional theory. It uses a conjugate-gradient algorithm applied to a variational expression from perturbation theory. The dielectric tensor, effective charges, and TO and LO phonons at $\mathbf{q}=0$ in α-quartz are obtained. A one-parameter scissors operator gives the dielectric tensor within 0.5% of the experimental value. The anisotropy of the effective charge tensor is shown to be crucial for reproducing the LO-TO splittings.

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Crystalline and vitreous silica (SiO_2) are systems of technological as well as fundamental interest, for which accurate experimental data and theoretical models are desirable. Recently there has been a flurry of activity in improving the parametrization of interatomic model potentials to describe silicas and other oxides, which is a problem with a long history [1]. There have also been numerous applications of powerful *ab initio* methods to study the structures and properties of α-quartz and other polymorphs [2–4]. Bonding topology and forces are intimately related to phonon frequencies and normal modes, so that high-quality theoretical calculations of phonons can strongly constrain the search for interatomic model potentials. In addition, a detailed understanding of the optical response of silica serves technological needs, for example, in the fabrication of optical waveguides.

In the present paper we propose a new technique for studying response functions in solids and use it to study the dielectric tensor, Born effective charges, and phonons in α-quartz, the simplest tetrahedrally bonded silica.

The use of density-functional theory (DFT) implemented within the local density approximation (LDA) [5] is well established as an effective tool in studying the electronic structure and total energy of solids with no parametrization to experimental data [6]. Recent advances in linear response theory by Baroni, Giannozzi, and Testa (BGT) [7] permit calculation of response functions in solids by use of the same reliable theory, without some of the drawbacks of previous methods [8] (i.e., no use of supercells). The BGT method has been used widely in calculations of linear-response functions, including phonon frequencies, elastic, dielectric, and piezoelectric constants, and optical response in various materials; also thermal expansion of Si [9–12]. A general formalism for nonlinear responses has been derived using the "$2n+1$" theorem of perturbation theory [13].

Our method improves on the BGT method by using a *variational* expression for the coefficients of these response functions, and also by replacing the traditional diagonalization procedure performed within a self-consistent density loop by a conjugate-gradient algorithm [14] where the diagonalization and self-consistency steps are done simultaneously [15]. This new method is especially attractive to use when there are more than four atoms in the unit cell of the unperturbed system: Implemented with fast Fourier transforms and separable pseudopotentials [2,16], the scaling of the computational effort is no worse than $N_{\text{band}}N_{\text{pw}}\ln N_{\text{pw}}$ or $N^2_{\text{band}}N_{\text{pw}}$ for a large unit cell, where N_{band} is the number of *occupied* bands in the problem, and N_{pw} is the number of plane waves in the basis.

The very existence of a formulation of the DFT total energy that is variational with respect to wave functions is important in the current practice of *ab initio* calculations [6]. In the present Letter we introduce the following expression for the second-order perturbation of the DFT total energy, which is variational with respect to *first-order perturbations* of the wave functions [17]. We follow the notation of Ref. [13]:

$$E^{(2)}\{\psi_\alpha^{(0)};\psi_\alpha^{(1)}\} = \sum_{\alpha,\text{occupied}} [\langle\psi_\alpha^{(0)}|v_{\text{ext}}^{(1)}|\psi_\alpha^{(1)}\rangle + \langle\psi_\alpha^{(1)}|v_{\text{ext}}^{(1)}|\psi_\alpha^{(0)}\rangle + \langle\psi_\alpha^{(1)}|(H^{(0)}-\varepsilon_\alpha^{(0)})|\psi_\alpha^{(1)}\rangle]$$
$$+\frac{1}{2}\int \frac{\partial^2 E_{\text{Hxc}}}{\partial n(\mathbf{r})\partial n(\mathbf{r}')} n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' + E^{(2)}_{\text{Nonvar}} + E^{(2)}_{\text{Ewald}}\,, \tag{1}$$

where

$$E^{(2)}_{\text{Nonvar}} = \sum_{\alpha,\text{occupied}} \langle\psi_\alpha^{(0)}|v_{\text{ext}}^{(2)}|\psi_\alpha^{(0)}\rangle \tag{2}$$

is a functional of the ground-state wave functions $\psi_\alpha^{(0)}$ only, and $E^{(2)}_{\text{Ewald}}$ is the second-order perturbation of the Ewald energy part of the total energy. $E^{(2)}$ is variational with respect to $\{\psi_\alpha^{(1)}\}$, with the constraint that

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$$\langle \psi_\beta^{(0)} | \psi_\alpha^{(1)} \rangle = 0 \qquad (3)$$

for all α and β labeling occupied states. The first-order density $n^{(1)}(\mathbf{r})$ is given by

$$n^{(1)}(\mathbf{r}) = \sum_{\alpha,\text{occupied}} \psi_\alpha^{(0)*}(\mathbf{r})\psi_\alpha^{(1)}(\mathbf{r}) + (\text{c.c.}) \,. \qquad (4)$$

In Eqs. (1)-(4) the ground-state wave functions $\psi_\alpha^{(0)}$ are fixed, having been computed in a separate unperturbed ground-state calculation.

The computational effort to minimize $E^{(2)}$ is similar to the effort needed to minimize the ground-state total energy in the conjugate-gradient method [14] and is often even less. Specializing Eqs. (1)-(4) to a phonon perturbation with wave vector $\mathbf{q}$, in which atom τ is moved in direction i, or an electric field perturbation along direction j, is done by analogy with the procedure presented in Refs. [9,13]. Once the first-order wave functions $\psi_\alpha^{(1)}$ for all phonon polarizations i at a given $\mathbf{q}$ or all electric field directions j have been obtained, the matrix elements of the dynamical matrix $D_{i_1\tau_1;i_2\tau_2}(\mathbf{q})$, the Born effective charge tensor $Z^*_{\tau,ij}$, and the electronic dielectric tensor $\varepsilon_{\text{el}}^{j_1,j_2}$ (sometimes called $\varepsilon_\infty^{j_1,j_2}$) are easily computed. A more complete description of the method, a generalization of the variational properties to higher order, and a discussion of the relationship with the $2n+1$ theorem of perturbation theory [13] will be presented elsewhere [18].

In our α-quartz calculations, the atomic potentials plus core electrons are replaced by extended norm-conserving separable *ab initio* pseudopotentials [19]. We use a rational polynomial parametrization [20] of the exchange-correlation functional, which is based on the Ceperley-Alder [21] electron-gas data. In what follows we will present results obtained with one special $\mathbf{k}$ point at $\mathbf{k}=(\frac{1}{3},0,\frac{1}{4})$ and a kinetic energy cutoff of 30 hartrees (about 5600 plane waves). Plane waves up to a kinetic energy cutoff of 22.5, 25, 27.5, and 30 hartrees, as well as Brillouin zone integration on special point grids of 1, 2, and 6 special $\mathbf{k}$ points [22], have been studied in order to estimate convergence errors.

The unit cell of α-quartz has nine atoms with space-group trigonal $P3_221$ [23]. For every given $\mathbf{k}$-point set and kinetic energy cutoff we have determined the equilibrium geometry by minimizing the LDA ground-state total energy; then we have studied phonon and electric field perturbations. For one special $\mathbf{k}$ point and 30 hartrees, the lattice constants are found to be $a=9.099$ bohrs and $c=10.057$ bohrs [basis set convergence (BSC) and Brillouin zone integration (BZI) error less than 0.1% and 0.5%, respectively], and the internal atomic coordinates are Si, $u=0.4614$ and O, $x=0.4098$, $y=0.2815$, and $z=0.1081$ (BSC and BZI errors in absolute numbers less than 0.0004 and 0.003, respectively). Experimental values are [24] $a=9.290$, $c=10.215$, $u=0.4697$, $x=0.4135$, $y=0.2669$, and $z=0.1191$.

Using the predicted geometry, we have computed the electronic contribution to the dielectric tensor. Along the trigonal axis we find $\varepsilon_{\text{el}}^{j_1,j_2}=2.566$ while perpendicular the value is 2.527 (BSC and BZI errors less than 0.2% and 1%, respectively). The corresponding experimental values are 2.383 and 2.356 [25]. The theoretical overestimation due to LDA is well known, and can be corrected semiempirically by including a single-parameter "scissors operator" [10]. Inclusion of a scissors shift $\Delta=1.8$ eV, corresponding to the LDA gap underestimate in α-quartz [4], leads to the very satisfactory values 2.385 and 2.353. Note that with or without a scissors correction, the slight anisotropy in the dielectric tensor is well described. The above theoretical results all include local field corrections. Without local field corrections (and without the scissors correction) the parallel and perpendicular dielectric constants are 2.689 and 2.668, respectively, so local fields contribute about a 5% effect.

The predicted Born effective charge tensor for the O atom at position (x,y,z) and the Si atom at position $(u,0,0)$ is presented in Table I (BSC and BZI errors less than 0.01 and 0.02, respectively, for the value of any component of $Z^*_{\tau,ij}$). The effective charge tensors for every other atom can be obtained using the symmetry operations of the crystal. If α-quartz were purely ionic, with a fixed number of electrons following the nuclei as they move, we would obtain symmetric, diagonal, isotropic tensors equal to the ionic charge. This is clearly *not* the case for α-quartz. The importance of this nonionic behavior will be analyzed at the end of this paper.

Although this method can easily (without supercells) give the dynamical matrix at any phonon wave vector $\mathbf{q}$, we will restrict ourselves to $\mathbf{q}=0$ (the Γ point) [26]. The phonon frequencies at Γ present nonanalytic behavior due to the long-range Coulomb field. The limiting values for $\mathbf{q}\to 0$ along the trigonal axis and $\mathbf{q}\to 0$ parallel to it can be different. The modes at Γ occur in three symmetry representations: A_1, A_2, and E. Depending on the direction as $\mathbf{q}\to 0$, the A_2 and E modes occur as longitudinal modes A_{2L} and E_L or transverse modes A_{2T} and E_T [27]. Table II shows our results (BSC and BZI error less than

TABLE I. Theoretical Born effective charge tensor $Z^*_{\tau,ij}$. The coordinates of the atoms are Si$(u,0,0)$ and O(x,y,z) where u,x,y,z can be found in the text.

	Electric field direction		
	x	y	z
	Silicon atom		
Displacement along			
x	3.016	0.0	0.0
y	0.0	3.633	0.282
z	0.0	−0.324	3.453
	Oxygen atom		
Displacement along			
x	−1.326	0.429	0.222
y	0.480	−1.999	−0.718
z	0.298	−0.679	−1.726

0.5% and 1.5%, respectively, except the first A_1 mode [28]), and compares with experimental results at 0 K [25,29]. 23 of the 28 mode frequencies are within 3% of the experimental values, with a slight overall tendency to underestimation. Notable exceptions are the first A_1 mode which is overestimated by 9%, and the lowest A_{2T} and A_{2L} modes and the second lowest A_1 that are underestimated by about 6%. Nevertheless, the theoretical and experimental ordering of the levels is exactly the same.

Next we consider the role of ionic motion in the response of α-quartz to an electric field. The low-frequency dielectric tensor components are computed to be 4.979 along the trigonal axis and 4.776 perpendicular to it, to be compared with the experimental values of 4.64 and 4.43, respectively [25]. Including the scissors correction for the electronic dielectric tensor, without changing the LO and TO phonon frequencies, and using the generalized Lyddane-Sachs-Teller relation [25] leads to 4.628 and 4.448, respectively. Agreement with experiment is thus better than 0.5% for both the low- and high-frequency dielectric tensors. Note that the value of the one-parameter scissors correction was not adjusted to bring about agreement in the dielectric tensors; it is obtained from an independent source by adjusting the LDA band gap to the optical gap [4].

TABLE II. Phonon frequencies of α-quartz at 0 K at Γ (cm^{-1}).

Theory		Experiment[a]	
	A_1 modes		
238.9		219	
339.3		358	
461.7		469	
1061.2		1082	
TO	LO	TO	LO
	A_2 modes		
341.4	365.7	361.3	385
493.4	540.5	499	553
762.4	784.7	778	791
1056.5	1218.3	1072	1230
	E modes		
133.3	133.4	133	133
261.3	263.2	269	269
377.6	389.2	393.5	402
443.8	498.6	452.5	512
690.8	694.5	698	701
791.7	803.9	799	811.5
1045.0	1209.5	1066	1227
1128.1	1123.9	1158	1155

[a] These data were extrapolated from the temperature-dependent experimental values provided by Ref. [25] (for the six highest E modes and the A_2 modes) and by Ref. [29] (two lowest E modes and the A_1 modes) using a $\omega(T)=\omega_0+aT^{1.8}$ law as advocated in the latter paper.

Let us now analyze in more detail the LO-TO splittings. These splittings are due to the coupling of the atomic displacement with the long-range electric field by means of the Born effective charge tensor. This tensor $Z^*_{\tau,ij}$ may be decomposed into three contributions: (1) a symmetric, isotropic tensor (the trace) $Z^*_\tau \delta_{ij}$, (2) the remaining symmetric traceless part $Z^{*S}_{\tau,ij}$, and (3) the antisymmetric part $Z^{*A}_{\tau,ij}$, where

$$Z^*_{\tau,ij}=Z^*_\tau \delta_{ij}+Z^{*S}_{\tau,ij}+Z^{*A}_{\tau,ij}\,, \tag{5}$$

with $\sum_i Z^{*S}_{\tau,ii}=0$, $Z^{*S}_{\tau,ij}=Z^{*S}_{\tau,ji}$, and $Z^{*A}_{\tau,ij}=-Z^{*A}_{\tau,ji}$. τ indexes atoms in the unit cell, i represents the Cartesian direction of an electric field, and j represents the direction of atomic displacement. The antisymmetric contribution is seen to be large for the Si atoms, while the traceless symmetric part is large for the O atom. From Table II we have extracted the values of the LO-TO splittings shown in Table III (BSC and BZI error for LO-TO splittings are less than 3% and 10%, respectively, except for the lowest E mode [30]). There is good agreement between the experimental and theoretical values for the LO-TO splittings using the full $Z^*_{\tau,\alpha\beta}$. When we suppress the antisymmetric part, the agreement is seen to be slightly worse. When the full tensor is replaced by the symmetric, isotropic part $Z^*_\tau \delta_{\alpha\beta}$, with $Z^*=-1.684$ for O and 3.368 for Si, this agreement with experiment is now completely destroyed: some LO-TO splittings are much too large; some are much too small. Even if we try to adjust the value of the isotropic charge, the LO-TO splittings cannot be matched. As mentioned above, this effect is a direct consequence of the nonionicity of the

TABLE III. LO-TO splittings at Γ in α-quartz (cm^{-1}). (a) Experimental data extrapolated to 0 K, (b) theoretical results using the full effective charge tensor, (c) the same as (b) using only the symmetric part of the effective charge tensor, and (d) the same as (b) using only the trace of the effective charge tensor.

(a) Experiment	(b) Full Z^*	(c) Symmetric Z^*	(d) Trace-only Z^*
	$A2$ modes		
24	24.3	26.3	44.5
54	47.1	38.9	82.3
13	22.5	29.4	45.9
158	161.9	149.4	97.6
	E modes		
	0.15	0.25	0.69
	1.9	2.2	4.5
8.5	11.7	10.9	14.3
60	54.8	51.8	104.5
3	3.7	5.6	8.0
12.5	12.2	13.3	26.4
161	164.5	165.7	115.0
−3	−4.2	−5.9	−11.9

binding in the α-quartz crystal. No simple charged ball (*isotropic* rigid ion) type model interatomic potential [1] will be able to reproduce accurately the LO-TO splittings, and, in consequence, the entire phonon spectrum of α-quartz, without large, unphysical modification of the short-range interatomic forces.

To summarize, the present method provides an efficient way to compute the dielectric tensor, effective charges, and full dynamical matrix at any wave vector **q** for an arbitrary unit cell, within LDA, for any material. Without any *a priori* model of interatomic forces, we have been able to predict the properties in α-quartz by *ab initio* means, and have obtained excellent agreement with experiment. The use of a one-parameter scissors correction yields dielectric tensors within 0.5% of experimental values. The significant role of Born effective charge tensor anisotropy in giving the correct LO-TO splitting has been emphasized.

Finally, note that the ability to compute the dynamical matrix at arbitrary **q** permits conducting a Brillouin zone summation to get force constants in real space [31], and opens the way to *ab initio* calculation of thermodynamical properties [12].

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