

Raman tensor calculated from the $2n+1$ theorem in density-functional theory

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In this work we present a method to determine the Raman coefficients of tetrahedrally bonded semiconductors directly in density-functional theory. For this purpose we apply the $2n+1$ theorem to derive an analytical expression for the Raman tensor. To the best of our knowledge, this is the first *ab initio* application of the $2n+1$ theorem involving mixed third-order derivatives of the total energy in terms of phonon displacements and electric fields. Numerical results are given for Si, Ge, and various III-V compounds. Furthermore we compare our results with those obtained by frozen-phonon-like calculations and experimental data where available. Our approach can be easily extended to the calculation of Raman tensors for larger systems with other symmetries.

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Density-functional perturbation theory (DFPT) has been applied successfully to the first-principles determination of linear-response properties of materials.¹ But there exists a large number of nonlinear effects. Examples for this are the lifetimes of phonons, the second-harmonic generation, and the Raman effect. This last effect is theoretically determined entirely by the phonon density of states (DOS) and by the Raman tensor. The DOS can easily be calculated by standard linear DFPT.

Thanks to the so-called $2n+1$ theorem² within DFPT, third-order response function is accessible. First applications have demonstrated very good results, but these applications are restricted to derivatives of the total energy with respect either to only atomic displacements,³ i.e., the anharmonic force constants, or to only a homogeneous electric field,^{4,5} i.e., the nonlinear susceptibilities. No mixed third-order derivatives have been evaluated with the use of the $2n+1$ theorem yet. But these quantities can be obtained, in principle, from the knowledge of the Kohn-Sham wave functions and Hamiltonians to first order in an atomic displacement and an electric field. In the following we focus on the Raman tensor, which is the third-order response function with respect to an atomic displacement and two electric fields.

Up to now the Raman tensor has been calculated by frozen-phonon techniques.⁶ These techniques are, in principle, less accurate and require extended computational effort.

Our new approach allows the formulation of a general analytical expression for the Raman tensor. We demonstrate how the technical difficulties can be mastered by evaluating this formula. Finally we present the first calculation of Raman tensors via the $2n+1$ theorem for the elemental semiconductors silicon and germanium as well as for a number of III-V semiconductors. To validate our approach we compare our results with those which we obtain by frozen-phonon-like calculation.

The Raman tensor \mathbf{P} is defined as the third-order derivative of the total energy \mathcal{E} with respect to an atomic displacement \mathbf{u}^κ and twice a homogeneous electric field \mathbf{E} ,

$$\varepsilon_0 P_{\alpha\alpha'}^\kappa|_{\alpha''} = \frac{\partial^3 \mathcal{E}}{\partial E_\alpha \partial E_{\alpha'} \partial u_{\alpha''}^\kappa}. \quad (1)$$

In the framework of density-functional theory the Hamiltonian is given by

$$H^{(0)} = T + v_{\text{ion}} + v_{\text{Hxc}}, \quad (2)$$

where T is the kinetic-energy operator, v_{ion} the ionic contribution to the potential, and v_{Hxc} the sum of the Hartree, exchange, and correlation potentials. Changing from the Bloch orbitals to the periodic parts $|u_{v\mathbf{k}}\rangle$ of them, the eigenvalue equation becomes

$$H_k^{(0)}|u_{v\mathbf{k}}\rangle = \varepsilon_{v\mathbf{k}}|u_{v\mathbf{k}}\rangle, \quad (3)$$

where $H_k^{(0)} = e^{-i\mathbf{k}\cdot\mathbf{r}} H^{(0)} e^{i\mathbf{k}\cdot\mathbf{r}}$ is the periodic Hamiltonian. Under the action of an external electric field \mathbf{E} the Hamiltonian is given by

$$H = H^{(0)} + e\mathbf{E}\cdot\mathbf{r}. \quad (4)$$

Based on the modern theory of polarization⁷⁻⁹ the Hamiltonian (4) can be transformed to¹⁰

$$H_k = H_k^{(0)} + e\mathbf{E}\cdot\left(i\frac{\partial}{\partial\mathbf{k}}\right). \quad (5)$$

In this case the first-order Hamiltonian with respect to an electric field is simply given by

$$\frac{\partial H_k}{\partial E_\alpha} = \frac{\partial H_k^{(0)}}{\partial E_\alpha} + ie\frac{\partial}{\partial k_\alpha}. \quad (6)$$

Substituting this into the formula of Debernardi and Baroni¹¹ for the third-order response function and after some algebraic manipulation one eventually obtains

$$\frac{\varepsilon_0}{\Omega} P_{\alpha\alpha'}^\kappa|_{\alpha''} = \Pi_{\alpha\alpha'}^\kappa|_{\alpha''} + \Pi_{\alpha'\alpha}^\kappa|_{\alpha''}, \quad (7)$$

with

$$\begin{aligned}
\Pi_{\alpha\alpha'}^{\kappa} = & \sum_{v,v'} \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} \delta_{v,v'} \left(4 \left\langle \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha}} \left| \mathcal{P}_c \frac{\partial v_{Hxc}}{\partial E_{\alpha'}} \right| \mathcal{P}_c \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha''}} \right\rangle \right. \\
& + 2 \left\langle \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha}} \left| \mathcal{P}_c \frac{\partial v_{KS}}{\partial E_{\alpha''}} \right| \mathcal{P}_c \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha'}} \right\rangle \left. \right) \\
& - \left(2 \left\langle \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha}} \left| \mathcal{P}_c \frac{\partial u_{v'\mathbf{k}}}{\partial E_{\alpha'}} \right\rangle \left\langle u_{v'\mathbf{k}} \left| \frac{\partial v_{KS}}{\partial E_{\alpha''}} \right| u_{v\mathbf{k}} \right\rangle \right. \right. \\
& + 4 \left\langle \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha''}} \left| \mathcal{P}_c \frac{\partial u_{v'\mathbf{k}}}{\partial E_{\alpha}} \right\rangle \left\langle u_{v'\mathbf{k}} \left| \frac{\partial v_{Hxc}}{\partial E_{\alpha'}} \right| u_{v\mathbf{k}} \right\rangle \left. \right) \\
& + 2 \left\langle u_{v\mathbf{k}} \left| \frac{ie\partial}{\partial k_{\alpha}} \right| \left(\left| u_{v'\mathbf{k}} \right\rangle \left\langle \frac{\partial u_{v'\mathbf{k}}}{\partial E_{\alpha'}} \right| \mathcal{P}_c \right) \mathcal{P}_c \frac{\partial u_{v\mathbf{k}}}{\partial E_{\alpha''}} \right\rangle \\
& + \frac{1}{2} \int d^3r f_{xc}^{\text{LDA}}(\mathbf{r}) \frac{\partial n(\mathbf{r})}{\partial E_{\alpha}} \frac{\partial n(\mathbf{r})}{\partial E_{\alpha'}} \frac{\partial n(\mathbf{r})}{\partial E_{\alpha''}}, \quad (8)
\end{aligned}$$

where $\mathcal{P}_c = 1 - \sum_v |u_{v\mathbf{k}}\rangle\langle u_{v\mathbf{k}}|$ is the projector on the unperturbed conduction-band subspace and

$$f_{xc}^{\text{LDA}}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'') \frac{\partial^3 E_{xc}[n^{(0)}]}{\partial n(\mathbf{r}) \partial n(\mathbf{r}') \partial n(\mathbf{r}'')} \Big|_{n=n^{(0)}}$$

the third-order exchange and correlation functional in the local density approximation (LDA). $n^{(0)}$ is the unperturbed charge density. The projected orbitals perturbed by some λ are given by the Sternheimer equation,

$$[H_{KS}(\mathbf{k}) - \varepsilon_v(\mathbf{k})] \mathcal{P}_c \left| \frac{\partial u_{v\mathbf{k}}}{\partial \lambda} \right\rangle = -\mathcal{P}_c \frac{\partial v_{KS}(\mathbf{k})}{\partial \lambda} |u_{v\mathbf{k}}\rangle. \quad (9)$$

The numerical evaluation of Eq. (8) includes the summation over special \mathbf{k} points. For the finite differences we adopt the formula used by Marzari and Vanderbilt,¹²

$$\nabla f(\mathbf{k}) \equiv \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})], \quad (10)$$

where \mathbf{b} are the vectors connecting a \mathbf{k} point with its neighbors and $w_{\mathbf{b}}$ are associated weights. We decided to use this formula for two different reasons. One is the elegant way of using the full symmetry of the crystal. On the other hand it is very easy to change the length of the \mathbf{b} vectors. So the accuracy of the finite difference formula can be treated totally independent of the \mathbf{k} -point mesh. There occurs no problem with the arbitrary phases of the Bloch orbitals or with a general gauge-transformation, since $\partial/\partial k_{\alpha}$ acts only on gauge-invariant quantities.

Due to the symmetry of the diamond and zinc-blende structure the Raman tensor reduces to

TABLE I. Raman tensor element P in \AA^2 .

System	$2n+1$ theorem	Frozen phonon	Experiment
Ge	66.37	59.45	68 ± 14^a
Si	23.56	20.44	23 ± 4^b
AlP	5.13	4.44	
AlAs	7.39	5.64	
AlSb	16.44	14.68	
GaP	11.38	9.48	
GaAs	24.16	20.99	
GaSb	65.94	60.35	
InP	13.85	11.81	
InAs	67.44	52.54	
InSb	70.51	65.55	

^aReference 14.

^bReference 15.

$$P_{\alpha\alpha'\alpha''}^{\kappa} = (-1)^{\kappa} |\epsilon_{\alpha\alpha'\alpha''}| P, \quad (11)$$

where ϵ is the totally antisymmetric Levi-Civita unit tensor. We have used an $8 \times 8 \times 8$ Monkhorst and Pack¹³ special \mathbf{k} -point mesh and an energy cutoff of 24 Ry. For the representation of the finite differences the \mathbf{b} vectors in Eq. (10) were chosen to have the length $(2\pi/a_0) \cdot 0.002 \cdot \sqrt{3}$. All these values ensure a good convergence.

As a test of our calculation of the acoustic sum rule ($\sum_{\kappa} P_{\alpha\alpha'\alpha''}^{\kappa} = 0$) we obtain the value 23.98 \AA^2 for Ga and -24.33 \AA^2 for As in GaAs. The deviation from the sum rule is therefore less than 2%. We assign this error to the numerical noise.

In Table I the results of our calculation for tetrahedrally bonded semiconductors are shown. Compared with the experimental data, which to our knowledge are available only for the elemental semiconductors, our results are excellent. We have also performed frozen-phonon-like calculations, where the third-order coefficient is evaluated by a numerical differentiation of the susceptibility with respect to an atomic displacement. Comparing these results we recognize that all the directly evaluated values are larger than the ones obtained by frozen-phonon techniques. From the dependence of the matrix element P on the frozen-phonon displacement we can exclude any influence of higher-order terms. At present the different results from the two methods is not clear to us and is left to future investigation. In the case of anharmonic force constants no such discrepancy can be seen.

We finally conclude that we have demonstrated a method for calculating the Raman tensor in DFPT.

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