Optical Activity of Selenium: A Nearly First-Principles Calculation

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For optical activity, we have derived a band-theoretic formula and evaluated it within the self-energy-corrected local-density-approximation approach using a plane-wave basis. For optically uniaxial, trigonal selenium, we compute (i) ρ, the optical rotatory power for propagation along the optic axis, (ii) g_{11}, a gyration tensor component, (iii) d_{11} for second-harmonic generation, and (iv) ε_e and ε_o, the two dielectric constants. These comprehensive results are the first reported in the literature for any crystal, and they agree with some, but not all, available measurements which are often not consistent with each other.

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When light travels through a medium, the material response may be characterized by the induced polarization. The polarization **P** may be written as a double power series in the electric field **E** and the wave vector of propagation **q**:

$$P_i = \frac{\varepsilon_{ij}-1}{4\pi} E_j + \chi^{(2)}_{ijl} E_j E_l + \cdots + i\eta_{ijl} q_j E_l + \cdots , \qquad (1)$$

where ε is the dielectric tensor, $\chi^{(2)} = 2d$ is the nonlinear susceptibility for second-harmonic generation, and η is the optical activity tensor [1]. The expansion unifies a host of optical phenomena, including the dielectric function, second-harmonic generation, optical activity, and higher interactions such as third-harmonic generation $[O(E^3)]$ and second-harmonic generation in centrosymmetric crystals $[O(qE^2)]$.

Optical activity is the primary subject of this paper. We present (i) a brief discussion of the phenomenology of optical activity; (ii) a review of the method [2,3] we have used successfully for ε and $\chi^{(2)}$, with new calculations for selenium; (iii) a formula for evaluating the optical activity tensor, with a discussion of our neglect of local-field corrections; and (iv) the results of a calculation of optical activity directly from the band structure on a nearly "first-principles" basis, with comparison to experiment. We are not aware of any similarly comprehensive calculation in the scientific literature for any crystal.

Theoretically, optical activity is of interest because it is the simplest phenomena which requires a transverse wave (i.e., use of the electromagnetic vector potential **A**) for its description. We select trigonal selenium for study because it has a simple crystal structure (three atoms per unit cell forming a helix), it is a semiconductor, and has a relatively [4] large (and hence measurable) optical rotary power.

Circular birefringence—that is, optical activity—has, in the absence of linear birefringence, eigenmodes of left and right circularly polarized light. This condition—circular, but no linear, birefringence—is achieved for propagation along the optic axis of a uniaxial crystal. In the case of trigonal selenium, the c axis (a threefold rotation axis) is the optic axis of this uniaxial crystal [5]. The plane of polarization of linearly polarized light propagating along that axis will be rotated by an amount ρ per unit length. The optical rotary power ρ is related to the optical activity tensor η by

$$\rho = \tfrac{1}{2}\alpha\omega(n_+ - n_-) = \alpha^2\omega^2\eta_{231} , \qquad (2)$$

where ω is the photon energy, α is the fine-structure constant, and $n_\pm$ are the indices of refraction for left (+) and right (−) circularly polarized light [6].

Our method is a simple modification of the Kohn-Sham local-density approximation (LDA). The LDA is by far the most widely used approximation used for the calculations of properties of real solids; the list of its successes is both long and familiar [7]. Nevertheless, by the early 1980s it became apparent that the local-density approximation underestimated band gaps in semiconductors by about 1 eV. This observation catalyzed the implementation [8–10] of the *GW* approximation to quasiparticle energies proposed by Hedin [11]. In brief, the *GW* approximation is Hartree-Fock theory with dielectric screening. *GW* band gaps are accurate within about 0.1 eV of the experimental values. Curiously, it was discovered that the LDA wave functions were in nearly perfect agreement with the *GW* quasiparticle wave functions even though the eigenvalues could differ by about 1 eV. Given the central role played by dielectric screening in the theory, it was troublesome that it was not immediately apparent how to use the *GW* eigenvalues to calculate an improved dielectric function; the *GW* eigenvalues would lead to an apparent overcorrection of the dielectric function from too large (in LDA) to too small [2,9,12].

In response to this challenge, some of us proposed a new effective Hamiltonian [2]

$$H_{\mathbf{k}} = H^{\mathrm{LDA}}_{\mathbf{k}} + \Delta_{\mathbf{k}} P_{c\mathbf{k}} \qquad (3)$$

for the calculation of dielectric response. The LDA Hamiltonian is modified by a self-energy correction, known colloquially as a "scissors operator," which shifts the conduction-band eigenvalues upward by an amount $\Delta_{\mathbf{k}}$ while preserving the eigenfunctions. It has proved adequate to take Δ to be independent of $\mathbf{k}$. Fundamentally, momentum matrix elements arise from the expression

$\nabla_{\mathbf{k}} H_{\mathbf{k}}$. If $H_{\mathbf{k}} = \frac{1}{2}(\mathbf{k}+\mathbf{p})^2 + V(\mathbf{r})$, then $\nabla_{\mathbf{k}} H_{\mathbf{k}} = \mathbf{k}+\mathbf{p}$ [13]. The self-energy operator changes, i.e., renormalizes, the matrix elements via $\mathbf{p} \rightarrow \mathbf{p} + \nabla_{\mathbf{k}}(\Delta_{\mathbf{k}} P_{c\mathbf{k}})$. Even if Δ is independent of $\mathbf{k}$, the projection operator $P_{c\mathbf{k}}$ is not, and this leads to important theoretical consequences.

This theory has demonstrated agreement with experimental values of the dielectric constant within 4% for the following materials: Si, Ge [2], AlP, AlAs, GaP, GaAs [3], and α-quartz [14]. The predictions have been successfully extended to second-harmonic generation in III-V semiconductors [3], and the elasto-optic tensor in Si [15].

For this work, we performed a fully converged LDA ground-state calculation, using the *ab initio* pseudopotential of Hamann [16] and the Kleinman-Bylander construction [17]. The LDA ground state is determined with the method of Teter, Payne, and Allan [18]. We work with a plane-wave energy cutoff of 10 hartrees and 144 or 410 integration points in the irreducible Brillouin zone for the symmorphic subgroup of the point group of selenium, which is one-quarter of the full Brillouin zone. We choose a self-energy constant of $\Delta = 1.1$ eV to align our LDA band gap of 1.2 eV within the experimental values of 2.0–2.3 eV [19]. Methodologically, we would prefer to take the result from a *GW* calculation, but none is available. The Δ value of 1.1 eV is in the range of eigenvalue shifts reported for other semiconductors [9,10].

Results for the dielectric constant calculation are given in Table I. The experimental situation is more fluid than in the case of the cubic semiconductors. Nevertheless, our calculation for the static limit of the dielectric constant is within the relatively broad experimental range suggested by Palik [20].

Results for second-harmonic generation are presented in Table II. In contrast to the III-V semiconductors [3], the local-field correction leads to an enhancement in selenium. For this component, the agreement with experiment is quite acceptable: We find agreement within stated error bars with two of the four experiments. The most discrepant result is due to Sherman and Coleman [21] who suggest that their measurement is strongly affected by the presence of a lattice resonance near 43 meV (28 μm) which is not captured by our fixed-lattice calculation.

The optical activity tensor was derived by expanding the polarization in the wave vector $\mathbf{q}$ and the vector potential $\mathbf{A}$ (in the gauge in which the scalar potential vanishes). For the case of insulators, we derive and exploit a sum rule to avoid a divergence as $\omega \rightarrow 0$; the form presented in Eq. (4) is restricted to insulators. We display our result using a superscript notation due to Aspnes [22],

$$\eta_{ijl} = \eta_{ijl}^{cv} + \eta_{ijl}^{ccv} + \eta_{ijl}^{vvc}, \tag{4a}$$

$$\eta_{ijl}^{cv} = 4\pi\overline{\Omega}_0 \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^v \mathrm{Im}\{\langle n\mathbf{k}|H_{\mathbf{k},i}\mathcal{G}_{n\mathbf{k}}^c(\omega)H_{\mathbf{k},jl}|n\mathbf{k}\rangle - \hat{\mathbf{i}} \leftrightarrow \hat{\mathbf{l}}\}, \tag{4b}$$

$$\eta_{ijl}^{ccv} = 8\pi\overline{\Omega}_0 \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^v \mathrm{Im}\{\langle n\mathbf{k}|H_{\mathbf{k},i}\mathcal{G}_{n\mathbf{k}}^c(\omega)H_{\mathbf{k},l}G_{n\mathbf{k}}^c H_{\mathbf{k},j}|n\mathbf{k}\rangle - \hat{\mathbf{i}} \leftrightarrow \hat{\mathbf{l}}\}, \tag{4c}$$

$$\begin{aligned}\eta_{ijl}^{vvc} = 8\pi\overline{\Omega}_0 \int_{\mathrm{BZ}} d\mathbf{k} \sum_{nm}^v \mathrm{Im}\{&\langle n\mathbf{k}|H_{\mathbf{k},j}|m\mathbf{k}\rangle\langle m\mathbf{k}|H_{\mathbf{k},i}\mathcal{G}_{m\mathbf{k}}^c(\omega) \\ &\times[\omega^2 - (\epsilon_{m\mathbf{k}} - H_{\mathbf{k}})^2 - (\epsilon_{n\mathbf{k}} - H_{\mathbf{k}})^2 - (\epsilon_{m\mathbf{k}} - H_{\mathbf{k}})(\epsilon_{n\mathbf{k}} - H_{\mathbf{k}})]\mathcal{G}_{n\mathbf{k}}^c(\omega)H_{\mathbf{k},l}|n\mathbf{k}\rangle\},\end{aligned} \tag{4d}$$

where $\overline{\Omega}_0$ is the unit cell volume divided by $(2\pi)^3$, BZ is the full Brillouin zone,

$$H_{\mathbf{k},i} = \hat{\mathbf{i}} \cdot \nabla_{\mathbf{k}} H_{\mathbf{k}}, \quad H_{\mathbf{k},ij} = \hat{\mathbf{i}} \cdot \nabla_{\mathbf{k}} \hat{\mathbf{j}} \cdot \nabla_{\mathbf{k}} H_{\mathbf{k}},$$

$$\mathcal{G}_{n\mathbf{k}}^c(\omega) = G_{n\mathbf{k}}^c(\omega) G_{n\mathbf{k}}^c(-\omega) G_{n\mathbf{k}}^c(0),$$

and $G_{n\mathbf{k}}^c(\omega)$ is the independent-particle Green's operator for the state $|n\mathbf{k}\rangle$ at frequency ω, i.e.,

$$G_{n\mathbf{k}}^c(\omega) = \sum_m^c \frac{|m\mathbf{k}\rangle\langle m\mathbf{k}|}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}} + \omega}. \tag{5}$$

The symbols c and v refer to the conduction and valence bands, respectively. Each term of η_{ijl} is antisymmetric in i and l. In deriving this expression we have treated the electrons as independent and moving in an effective one-body potential.

The local-field corrections to optical activity are neglected. Local-field corrections to the dielectric and second-harmonic response for elemental and simple compound semiconductors are typically on the order of 10%. Our results for selenium are consistent with this rule, as seen in Tables I and II; the second-harmonic local-field correction is surprisingly large at +27%. We suppose the local-field correction to optical activity will be about the

TABLE I. The static dielectric constants of selenium. For the ordinary value, the polarization is in the basal plane, and for the extraordinary value, it is directed along the c axis. The designation ε_{00} implies the neglect of local-field corrections, and ε_1 indicates their inclusion. The experimental data are a low-frequency extrapolation of the IR-visible data as suggested by Palik [20].

	LDA		$\Delta = 1.1$ eV		
	ε_{00}	ε_1	ε_{00}	ε_1	Expt.
Ordinary	11.8	10.3	9.0	7.9	6.2–8.4
Extraordinary	16.4	15.2	12.3	11.5	10.2–13.7

TABLE II. The nonlinear susceptibility for second-harmonic generation $d_{11}=\frac{1}{2}\chi^{(2)}_{111}$. Only the magnitude is reported, since there is ambiguity in the literature concerning the sign conventions. The designation d_{11}^{long} is a calculation neglecting local-field corrections.

	ω (meV)	λ (μm)	d_{11}^{long} (pm/V)	d_{11} (pm/V)
LDA	0	∞	179	220
$\Delta=1.1$ eV	0	∞	78	97
Expt. [29]	113	10.6		210 ± 42
Expt. [25]	113	10.6		97 ± 25
Expt. [28]	113	10.6		80 ± 42
Expt. [21]	43	28		1840 ± 880

same size.

The putatively small local-field correction is formally difficult to compute. Optical activity is an intrinsically transverse phenomenon, so one must use the electromagnetic vector potential. The usual practice in dielectric response calculations is to work with a scalar potential as the external perturbation. In particular, the exchange correlation can be approximated by a linearization of the LDA about the ground-state density, i.e., by a term $(\delta V_{xc}/\delta\rho)\delta\rho$. Contributions from this term were included in the calculation of the dielectric constant and the nonlinear susceptibility for second-harmonic generation. However, to include exchange-correlation effects in the optical activity calculation requires a knowledge of $\delta \mathbf{A}_{xc}/\delta j$. The density-functional theory of currents and vector potentials is at a rudimentary state of development at present [23].

Results for the optical rotatory power ρ are presented in Fig. 1. We divide ρ by ω^2 to remove the trivial frequency dependence given in Eq. (2). We find that our calculation is in agreement with the data of Adams and Haas [24] and one of two points measured by Day [25]. Given the uncertainties of the data of Henrion and Eckart [26] and our theoretical uncertainties (e.g., neglect of local-field corrections, BZ integration errors, neglect of spin-orbit splitting, the assumption of the constant value $\Delta=1.1$ eV) we do not see a conclusive disagreement. We are in agreement with the sign of ρ as reported by Henrion and Eckart; the others do not report the sign. The discrepancy between the Adams and Haas and the Henrion and Eckart data sets is a factor of 2 to 6 depending on the frequency. The origin of this discrepancy is unclear; we note that materials preparation difficulties have prevented a definitive measurement of even the dielectric constants.

For frequencies small compared to the band gap [in fact for $(\omega/\omega_{\text{gap}})^2 \ll 1$] we expect η to attain some constant value, leading to $\rho \propto \omega^2$. Our calculated points are consistent with $\rho \propto \omega^{1.9}$ for $\Delta=1.1$ eV. The data of Day may be fitted by $\rho \propto \omega^{0.6\pm0.3}$, which is difficult to understand theoretically.

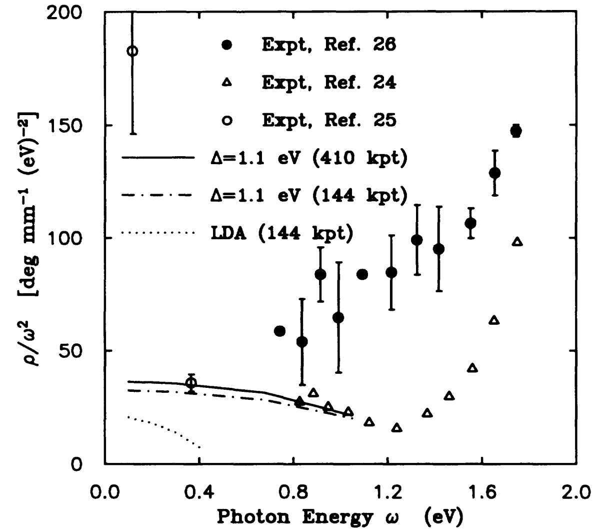

FIG. 1. The optical rotatory power ρ divided by ω^2 [which is suggested by Eq. (2)] of selenium for photon energies less than the direct band gap. We display the LDA result for 144 integration points (dotted line) and in the self-energy-corrected result with $\Delta=1.1$ eV for 144 (dash-dotted line) and 410 (solid line) integration points as a function of the photon energy ω (in eV). The sign of ρ is taken to be positive for Refs. [24] and [25].

We present our results only up to 1.05 eV. In this frequency regime, our results for the 144 and 410 k points are within 10% agreement. However, at higher frequencies, this agreement breaks down. Because the integrand becomes singular at the band gap, our uniform sampling

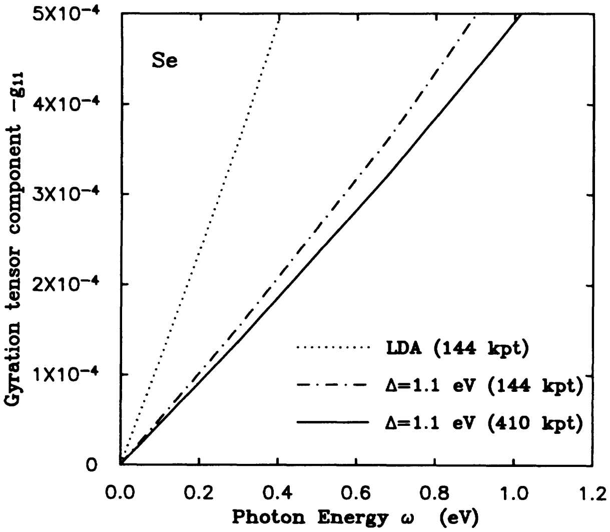

FIG. 2. The gyration tensor component $g_{11}=\alpha\omega\eta_{312}n_o$, where n_o is the ordinary refractive index. For the trigonal point group, η_{312} is the only independent tensor component other than the one η_{231} used to determine the optical rotatory power shown in Fig. 1.

method must fail at some frequency.

The prediction for the gyration tensor [5] component g_{11} is presented in Fig. 2. The self-energy correction to the LDA prediction reduces g_{11} by a factor of 3 at low frequencies and grows rapidly as the photon energy approaches the (wrongly placed) LDA band edge. To the best of our knowledge, g_{11} has not been measured for selenium. However, the predicted value is the same magnitude as KH_2PO_4 which has been measured [27].

To summarize, we presented a band-theoretic formula for optical activity and we have calculated the optical rotatory power for selenium along with a series of related optical properties: a gyration tensor component, the susceptibility for second-harmonic generation, and the dielectric constants. Our calculations are performed directly from a nearly first-principles band structure. The experimental input is limited to the dimensions of the unit cell and a self-energy correction of 1.1 eV to the band gap. Our calculations are in agreement with some data by Day [25] and with the measurement of Adams and Haas [24], but not those due to Henrion and Eckart [26]. For second-harmonic generation, we find agreement with the measurement of Day [25] and Patel [28] but not those of Jerphagnon, Batifol, and Sourbe [29].

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