

LiNbO₃ linear and nonlinear optical response from *first-principles* calculations

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Abstract—The dielectric function and second harmonic generation of ferroelectric LiNbO₃ is calculated from *first-principles*. Thereby we start from the electronic structure calculated within the density functional theory. The use of the GW approach to account for quasiparticle effects and the subsequent solution of the Bethe-Salpeter equation leads to a dielectric function that is in excellent agreement with the available experimental results. Our second harmonic generation calculations rest on the independent particle approximation and predict strong non-linear coefficients, in particular in the energy range starting from 1.5 eV.

Keywords: LiNbO₃, Theory, DFT, GW, Non-linear Optic, SHG

I. INTRODUCTION

The electro-optic, photo-refractive, and nonlinear optical properties of lithium niobate (LiNbO₃, LN) are exploited in a number of devices such as modulators for fiber-optic communications systems or holographic applications. LN, see Refs. [1, 2] for tutorial papers on its physical properties, occurs in two phases of trigonal symmetry with ten atoms per unit cell. The ground-state is ferroelectric with space group $R3c$.

Given the vast range of LN applications, our knowledge about its electronic and optical properties is surprisingly limited. For example, we are not aware of a measured electronic band structure. The direct band gap of 3.78 eV for the ferroelectric phase – frequently cited in the literature – is actually concluded from optical experiments [3]. Therefore it is affected by electron-hole attraction effects, which may reduce the size of the actual band gap, i.e., the difference between the ionization energy and the electron affinity, substantially. The situation is additionally complicated by the fact that a number of different band gap values have been reported, all concluded from optical absorption experiments. They range from the indirect gap of 3.28 eV reported in Ref. [4] to values of 4.0 or 4.3 eV [5, 6]. Recent theoretical work suggests that the band gap to be substantially larger, of the order of 4.7 - 6.5 eV [7, 8]. The optical absorption experiments mentioned above as well as further studies, e.g., Ref. [9] focus mainly on the onset of the absorption. We are aware of only two studies that address the linear optical absorption in the vacuum ultraviolet (VUV) domain [10, 11]. Second harmonic generation (SHG) measurements for photon energies up to 3 eV have been made by Ref. [40,41].

On the other side, the theoretical understanding is also limited. Up to date, a number of first-principles studies are available on the LN structural and vibrational properties, see, e.g., Refs. [12–14], that basically explain the measured phonon modes. The structural and vibrational properties of LN surfaces have been explained recently by means of atomistic simulations [15–17]. Also, the ferroelectric phase transition was modeled with molecular dynamics [18]. Only few calculations, see, e.g. Ref. [19], address the optical and electronic properties. Most *first-principles* band-structure calculations, e.g., Refs. [14, 20], are based on a single-particle picture and neglect quasiparticle effects that typically widen the band gap between occupied and empty states by a large fraction of its value [21]. An early theoretical study by Ching *et al.* [22] indicates the importance of self-energy effects: Using the approximate Sterne-Inkson model [23], they predicted self-energy corrections of the order of one eV. However, the single-particle gap in Ref. [22] is much smaller (2.62 eV for the ferroelectric phase) than in the more recent studies [20] (3.69 eV) and [14] (3.48 eV). Recent work by Schmidt *et al.* [7] indeed indicates a very strong influence of excitonic and local-field effects on the LN optical absorption. While the calculations in Ref. [7] explain the essential features of the measured optical absorption [10, 11], their predictive power is limited, due to the use of a model dielectric function [24] for the description of the screened Coulomb interaction W in the GW approximation. In particular, the possible influence of lattice polarization effects [25] on the LN electronic and optical excitations could not be satisfactory clarified in Ref. [7]. Akkus *et al.* calculated the second harmonic generation response coefficients of LN and other ferroelectrics [42].

The present work goes significantly beyond previous theoretical work because for the first time the self-energy effects in the optical absorption are addressed from *first-principles*, i.e., in the random phase approximation (RPA). Additionally, we present SGH spectra calculated within the independent-particle approximation (IPA) [26]. The calculation of the optical absorption occurs in three steps: (i) We use density functional theory in generalized gradient approximation (DFT-GGA) to determine the electronic ground state of ferroelectric LN. (ii) The electronic quasiparticle spectrum is obtained within the GW approximation (GWA) [27] to the exchange-correlation self-energy, and finally (iii) the Bethe-Salpeter equation (BSE) is solved for coupled electron-hole excitations [28–30], thereby accounting for the screened

electron-hole attraction and the unscreened electron-hole exchange [31–33].

II. METHODS

In detail, we start from first-principles projector augmented wave (PAW) calculations, using the VASP implementation of the DFT-GGA [34, 35]. A $6 \times 6 \times 6$ k -point mesh is used to sample the Brillouin zone. The electron wave functions are expanded into plane waves up to an energy cutoff of 400 eV. The mean-field effects of exchange and correlation in GGA are modeled using the PW91 functional [36]. In the second step, we include electronic self-energy effects, i.e., replace the GGA exchange and correlation potential by the nonlocal and energy-dependent self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}'; E)$. We calculate Σ in the GW approximation [27], from the convolution of the single-particle propagator G and the dynamically screened Coulomb interaction W . Thereby we consider 608 electronic bands (30 valence bands and 587 conduction bands) to calculate the Green function G . The Coulomb interaction is calculated from first-principles, with the screening evaluated in the random phase approximation [39]. The electron-hole interaction is taken into account in the third step. The two-particle Hamiltonian

$$H_{vck, v'c'k'} = (\epsilon_{ck} - \epsilon_{vk}) \delta_{vv'} \delta_{cc'} \delta_{kk'} + 2 \int d\mathbf{r} d\mathbf{r}' \phi_{ck}^*(\mathbf{r}) \phi_{vk}(\mathbf{r}) \bar{v}(\mathbf{r} - \mathbf{r}') \phi_{c'k'}(\mathbf{r}') \phi_{v'k'}^*(\mathbf{r}') - \int d\mathbf{r} d\mathbf{r}' \phi_{ck}^*(\mathbf{r}) \phi_{c'k'}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \phi_{vk}(\mathbf{r}') \phi_{v'k'}^*(\mathbf{r}'), \quad (1)$$

describes the interaction of pairs of electrons in conduction states $|ck\rangle$ and holes in valence states $|vk\rangle$ [31–33]. The diagonal first part is given by the quasiparticle energies obtained in GW approximation. The second, the electron-hole exchange term, where the short-range part of the bare Coulomb potential $\bar{v}$ enters, reflects the influence of local fields. Finally, the third part, which describes the screened electron-hole attraction, is calculated using a model dielectric function as proposed by Bechstedt et al. [24]. Thereby we use the value $\epsilon_\infty = 7.01$, obtained from optical IPA calculations, as input parameter. For the actual calculation of the polarizability, we use the time-evolution implementation described in [37, 38]. For numerical reasons, the inclusion of many-body effects is not yet possible for calculations of the LN nonlinear optical properties. Therefore we present calculations based on the independent-particle approximation. In detail, we use the approach outlined in Ref. [26], specifically Eq. 32 for the calculation of the second-harmonic generation spectra.

III. RESULTS

In Fig. 1 we plot the electronic band structure and density of states of ferroelectric LiNbO_3 calculated within the DFT (solid lines) and with GW corrections (dotted lines). The direct band gaps at Γ of 3.39 eV (DFT) and 5.42 eV (DFT+GW) are in very good agreement with previous calculations [7]. Strictly speaking LN appears to have an indirect band gap, with the valence band maximum slightly off- Γ . However, the uppermost valence band is relatively flat, so that LN can be approxi-

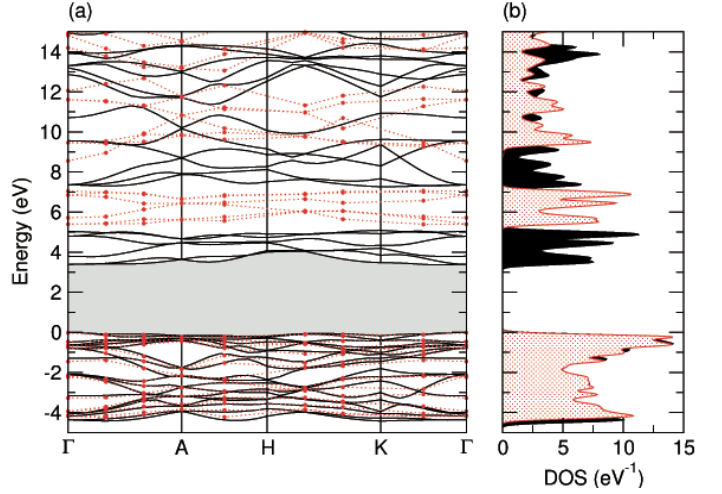


Figure 1. (color online) Electronic band structure (a) and density of states (b) of ferroelectric LN calculated within DFT-PW91 (solid lines, black) and GW correction (red circles, dotted shaded region). To guide the eye, the circles are connected by dotted lines. The gray region shows the main electronic band gap.

very regarded as a direct semiconductor at Γ . The electronic ground state in Fig. 1 is the starting point for the further calculations

In Fig. 2 we show the optical spectra calculated for ferroelectric LN according to the three levels of theory, i.e., DFT-GGA, GWA, and BSE. The spectrum obtained within DFT-GGA for ferroelectric LN agrees roughly with earlier independent-particle results [20, 22]. There are two main features of the optical absorption centered at about 5 and 8 eV. They arise from transitions between O $2p$ and Nb $4d$ states [7]. The inclusion of the many-body electron-electron interaction in GWA, i.e., the electronic self-energy, leads to a nearly rigid blue-shift of the spectra by about 2 eV.

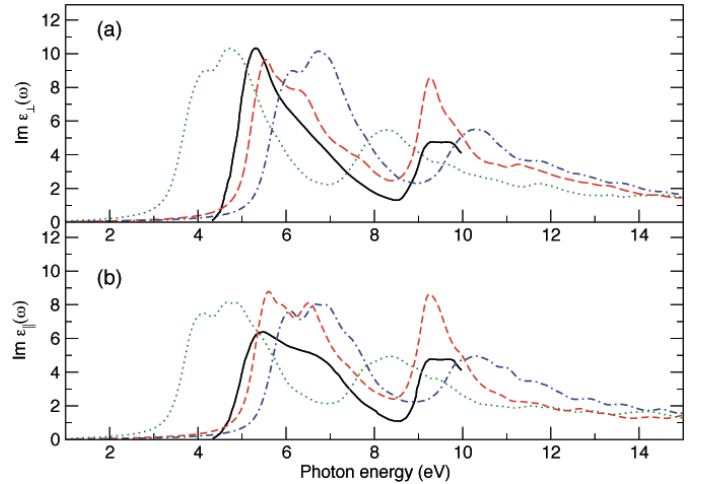


Figure 2. (color online) Imaginary part of the dielectric function of ferroelectric LN for (a) ordinary (perpendicular to c , $\epsilon_\perp$) and (b) extraordinary (parallel to c , $\epsilon_\parallel$) polarization calculated within the IPA (dotted), IQPA (dott-dashed) and BSE (with GW corrections) (dashed) compared to experimental measurements (solid) of Ref. [11].

The Coulomb correlation of electrons and holes, accounted for by solving the BSE, changes the line shape somewhat. The first peak of the low-energy main feature of the optical absorption becomes more pronounced and the whole feature is red-shifted compared to the GWA spectrum. It is now positioned at 5.5 or 5.6 eV for $\varepsilon_{\perp}$ or $\varepsilon_{\parallel}$, respectively. The oscillator strength of the originally rather broad (≈ 2 eV) high-energy main feature of the optical absorption is red-shifted and transferred into a single sharp peak at about 9.3 eV (for $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$). Compared to the experimental data for the ferroelectric LN, where absorption peaks at 5.3 – 6 and 9.2 – 10 eV are observed [10, 11], the inclusion of self-energy and excitonic effects improves the theoretical description substantially. This concerns both the peak positions and the line shapes, which sharpen due to the inclusion of excitonic effects. Interestingly, the experimental observation that the first absorption peak is broader for $\varepsilon_{\perp}$ than for $\varepsilon_{\parallel}$ in ferroelectric LN [11] is reproduced in the calculations that account for electron-hole interactions much more clearly than on the single-particle level of theory. Since in the present work no lattice polarization effects are taken into account, the excellent agreement between measured and calculated data suggests that they are of minor importance.

In Fig. 3 we report the SHG spectrum calculated within the IPA approximation. Shown are the real part, imaginary part, and absolute value of χ^2_{333} coefficients in the range up to 3 eV. Comparable experimental values for $d_{33} = |\chi^2_{333}|/2$ are given in Table 2 of Ref. [40]: The values $d_{33} = 34 - 42, 27, 25, 20$ pm/V for wavelength 1.058, 1.064, 1.150, and 1.318 μm are underestimated in our calculations (values between 8 and 10 pm/V have been obtained). While of the same order of magnitude than the data measured in Ref. [40], there are noticeable differences. While we note some scatter in the experimental results, we cannot, at present, exclude that the neglect of many-body effects and/or numerical limitations are responsible for these differences. Concerning the first, in Ref. [26] a strong impact of the electronic self-energy on the calculated SHG spectrum of GaAs was noted. Work is presently in progress to clarify the influence of self-energy effects on the SHG values calculated for LN.

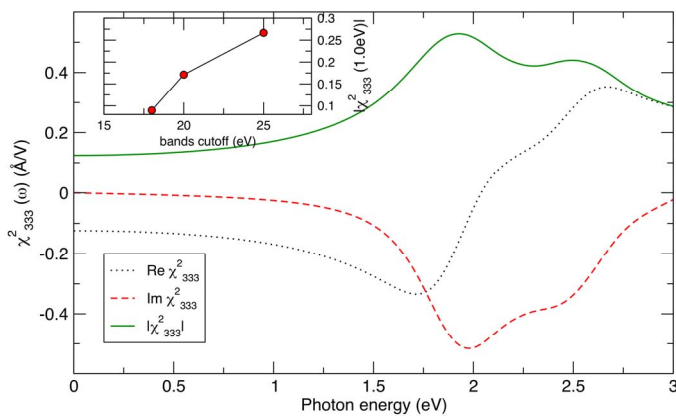


Figure 3. Real part, imaginary part, and absolute value of the χ^2_{333} coefficients of ferroelectric LiNbO₃ calculated within the IPA approximation. The inset shows dependence of $|\chi^2_{333}|$ at 1.0 eV on the bands cutoff T_B .

Concerning the numerical limitations, the deviation from the experiment is partially attributed to the strong dependence of the absolute value of χ^2_{333} on the number of contributing bands, which are determined by a bands cutoff $|\varepsilon_n(\mathbf{k}) - \varepsilon_n(\mathbf{k})| < T_B$ (see inset of Fig. 3). On the other hand the latter increases the numerical effort for the calculation of the SHG spectrum. Our data are in qualitative agreement with the calculations of Ref. [42].

To summarize, we performed first-principles calculations of the LiNbO₃ optical properties. In case of the calculated dielectric function a large influence of many-body effects is observed. In particular, strong excitonic effects with exciton binding energies of the order of 0.5 eV are predicted. The calculations are in excellent agreement with the available measured data. Also, calculated SHG spectra are present. Large optical anisotropies are predicted for photon energies starting from 1.5 eV.

ACKNOWLEDGMENT

The calculations were done using grants of computer time from the Paderborn Center for Parallel Computing (PC²) and the Höchstleistungs-Rechenzentrum Stuttgart. The Deutsche Forschungsgemeinschaft is acknowledged for financial support.

REFERENCES

- [1] A. Räuber, Current Topics in Materials Science **1**, 481 (1978).
- [2] R. S. Weis and T. K. Gaylord, Appl. Phys. A **37**, 191 (1985).
- [3] A. Dhar and A. Mansingh, J. Appl. Phys. **68**, 5804 (1990).
- [4] Z. Jiangou, Z. Shipin, X. Dingquan, W. Xiu and X. Guanfeng, J. Phys.: Condens. Matter **4**, 2977 (1992).
- [5] D. Redfield and W. J. Burke, J. Appl. Phys. **45**, 4566 (1974).
- [6] S. Kase and K. Ohi, Ferroelectrics **8**, 419 (1974).
- [7] W. G. Schmidt, M. Albrecht, S. Wippermann, S. Blankenburg, E. Rauls, F. Fuchs, C. Rödl, J. Furthmüller and A. Hermann, Phys. Rev. B **77**, 035106 (2008).
- [8] C. Thierfelder, S. Sanna, A. Schindlmayr and W. G. Schmidt, phys. stat. sol. (c) **7**, 362 (2010).
- [9] H. Li, G. Xu, G. Hu and X. Wang, Cryst. Res. Technol. **29**, 693 (1994).
- [10] A. M. Mamedov, M. A. Osman and L. C. Hajieva, Appl. Phys. A **34**, 189 (1984).
- [11] E. Wiesendanger and G. Günterodt, Sol. State Commun. **14**, 303 (1974).
- [12] V. Caciuc, A. V. Postnikov and G. Borstel, Phys. Rev. B **61**, 8806 (2000).
- [13] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. B **61**, 272 (2000).
- [14] M. Veithen and P. Ghosez, Phys. Rev. B **65**, 214302 (2002).
- [15] Sergey V. Levchenko and Andrew M. Rappe, Phys. Rev. Lett. **100**, 256101 (2008).
- [16] S. Sanna and W. G. Schmidt, Phys. Rev. B **81**, 214116 (2010).
- [17] W. Hahn A. Widhalm A. Zrenner S. Sanna, G. Berth and W. G. Schmidt, Ferroelectrics (accepted).
- [18] S. R. Phillpot and V. Gopalan, Appl. Phys. Lett. **84**, 1916 (2004).
- [19] A. M. Mamedov H. Akkus and S. Cabuk, Int. J. Nanoelectronics and Materials **3**, 53 (2010).
- [20] I. V. Kityk, M. Makowska-Janusik, M. D. Fontana, M. Aillerie and F. Abdi, J. Appl. Phys. **90**, 5542 (2001).
- [21] F. Bechstedt, in Festkörperprobleme/Advances in Solid State Physics, edited by U. Rössler (Vieweg, Braunschweig/Wiesbaden, 1992), Vol. 32, p. 161.

- [22] W Y Ching, Z-Q Gu, and Y-N Xu, Phys. Rev. B **50**, 1992 (1994).
- [23] S. J. Jenkins, G. P. Srivastava and J. C. Inkson, Phys. Rev. B **48**, 4388 (1993).
- [24] F. Bechstedt, R. Del Sole, G. Cappellini and L. Reining, Solid State Commun. **84**, 765 (1992).
- [25] F. Bechstedt, K. Seino, P. H. Hahn and W. G. Schmidt, Phys. Rev. B **72**, 245114 (2005).
- [26] R. Leitsmann, W. G. Schmidt, P. H. Hahn and F. Bechstedt, Phys. Rev. B **71**, 195209 (2005).
- [27] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
- [28] S. Albrecht, L. Reining, R. Del Sole and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998).
- [29] L. X. Benedict, E. L. Shirley and R. B. Bohn, Phys. Rev. Lett. **80**, 4514 (1998).
- [30] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **83**, 856 (1999).
- [31] L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966).
- [32] W. Hanke and L. J. Sham, Phys. Rev. B **12**, 4501 (1975).
- [33] W. Hanke and L. J. Sham, Phys. Rev. B **21**, 4656 (1980).
- [34] G. Kresse and J. Furthmüller, Comp. Mat. Sci. **6**, 15 (1996).
- [35] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- [36] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- [37] W. G. Schmidt, S. Glutsch, P. H. Hahn and F. Bechstedt, Phys. Rev. B **67**, 085307 (2003).
- [38] P. H. Hahn, W. G. Schmidt and F. Bechstedt, Phys. Rev. Lett. **88**, 016402 (2001).
- [39] M. Shishkin and G. Kresse, Phys. Rev. B **74**, 035101 (2006).
- [40] I. Shoji and T. Kondo and A. Kitamoto and M. Shirane and R. Ito, J. Opt. Soc. Am. B, **14**, 2268 (2002).
- [41] J. Seres, Applied Physics B: Lasers and Optics, **73**, 705 (2001).
- [42] H. Akkus, S. Cabuk, A.M. Mamedov, Int. J. Nanoelectronics and Materials **3**, 53 (2010).