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Electrical and optical properties of $LiNbO_3$ single crystals at room temperature

H. Chaib, T. Otto, and L. M. Eng*

Institute of Applied Photophysics, University of Technology Dresden, D-01062 Dresden, Germany

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The electrical and optical properties of lithium niobate ($LiNbO_3$) at room temperature are theoretically calculated by using a microscopic model based on the orbital approximation in correlation with the dipole-dipole interaction. It is found that both the electronic polarizabilities and the electronic hyperpolarizabilities have to be considered in this calculation in order to match both the spontaneous polarization and refractive indices with experimental data.

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I. INTRODUCTION

Lithium niobate ($LiNbO_3$) falls among the most known technologically relevant ferroelectric oxide materials because of its remarkable optical anisotropy,[1–5] large spontaneous polarization,[2,6,7] electro-optical and nonlinear optical activity,[8–10] as well as the outstanding nonlinear optical properties for instance in periodically poled optical superlattices (PPLN's).[11–13] Its ferroelectricity was discovered as early as 1949. In contrast to many other ABO_3 ferroelectric oxides, $LiNbO_3$ has only two phases both being rhombohedral: the high temperature phase is centrosymmetric paraelectric, while the other one is noncentrosymmetric ferroelectric stable below the Curie temperature $T_C = 1210\,^\circ C$.

Here we present a somewhat different theoretical approach for studying the spontaneous polarization and refractive indices of $LiNbO_3$ at room temperature. Our microscopic model takes into account the anisotropy in the electronic polarizability and hyperpolarizability of all constituent ions, their ionic shifts, as well as the crystalline deformations. The model was previously tested for the calculation of bulk properties of monodomain tetragonal perovskites like $BaTiO_3$ and $KNbO_3$, i.e., their ferroelectricity and optical anisotropy as well as their linear electrooptical coefficients.[14–16] Furthermore, the same model was successfully applied for modeling electrical and optical properties within ferroelectric domain walls in $BaTiO_3$.[17] Based on those experiences which agree excellently well with the corresponding experimental data, we initiate here the application of this model to $LiNbO_3$ which shows a much more complicated structure than the tetragonal perovskites.

In this model, we account for the following points:

(i) expanding the local electric field by considering its components in all directions at once;

(ii) representing the local electric field in a tensorial equation which allows the description of all its components for all ions simultaneously;

(iii) developing the orbital approximation by taking into account the anisotropy in the electronic polarizability and electronic hyperpolarizability;

(iv) considering the correlation between the electronic polarizability and the electronic hyperpolarizability on one hand, and their dependence on the local electric field on the other hand (since these magnitudes are mutually dependent).

In a previous theoretical work, Kinase *et al.*[18] studied the ferroelectricity in $LiNbO_3$ by considering the local electric field of all ions to be aligned parallel to the direction of the spontaneous polarization, which actually is not the case in this compound as experimentally concluded by Reznik, Anikiev, and co-workers in their work devoted to the optical damage in $LiNbO_3$.[19,20] By studying the vibrational spectra they showed that the component of the local electric field in the direction perpendicular to the direction of the spontaneous polarization is not negligible. The same result was theoretically proven by Yatsenko[21] when studying the anisotropy of the electronic polarizability of O^{2-} ions in stoichiometric $LiNbO_3$. However, in Yatsenko's work this anisotropy results from considering only five instead of ten structurally nonequivalent ions forming the primitive rhombohedral unit cell. In the calculation presented here, we will consider all 30 ions of the conventional hexagonal unit cell and show that only ten ions are nonequivalent.

The paper is structured as follows: Section II discusses the electronic polarizabilities and hyperpolarizabilities of the constituent ions of $LiNbO_3$ by using a quantum method based upon the orbital approximation. We discuss the dipole-dipole interaction due to the local electric field acting on the constituent ions taking into account the crystalline deformations and individual ionic shifts which are important in $LiNbO_3$. Section III then presents the results for the spontaneous local electric field, the electronic polarizability and the second-rank $\tilde{\sigma}$ tensor (representing the electronic hyperpolarizability multiplied by the local electric field), the spontaneous polarization, as well as refractive indices calculated for $LiNbO_3$ at room temperature. This section also contains the discussion of the above-mentioned findings.

II. DESCRIPTION OF THE MODEL

A. Orbital approximation

In order to compute the electronic polarizabilities and electronic hyperpolarizabilities of $LiNbO_3$, we use a quantum-mechanical approach based upon the orbital approximation. In this approach, each ion is considered as a combination of a core (inner electrons and nucleus) and a shell carrying the outer electron. The Hamiltonian of the core-shell system is written as

$$H = H_0 + H_1 \tag{1}$$

with

$$H_0=\frac{p^2}{2m}-\frac{Z}{R}e^2, \tag{2}$$

$$H_1=e\mathbf{E}\cdot\mathbf{R}, \tag{3}$$

where H_0 represents the Hamiltonian in the absence of the local field and H_1 can be considered as a perturbation. In Eq. (2), Z represents the effective charge of the core for the outer electron considered, while in Eq. (3) $\mathbf{E}$ represents the local electric field acting on a given ion, and $\mathbf{R}$ is the distance from the core to any point of the wave function describing the shell of this ion. We denote the wave function for $\mathbf{E}=0$ as ψ_0, and assume that the wave function of the core-shell system for $\mathbf{E}\neq 0$ may be expanded into a linear series of small perturbations in ψ_0. For this case, we introduce the variational parameter λ as

$$\psi(\lambda)=(1+\lambda\mathbf{E}\cdot\mathbf{R})\psi_0. \tag{4}$$

By using the variational principle $\partial I/\partial\lambda=0$, where I is the energy of the system, we can express λ by the following equation (see Appendix A):

$$\lambda=-\frac{2\sum_k E_k^2\langle x_k^2\rangle}{a_B e E^2}\left[1-\frac{4\left(\sum_k E_k^2\langle x_k^2\rangle\right)^3}{a_B^2e^2E^4}+\frac{32\left(\sum_k E_k^2\langle x_k^2\rangle\right)^6}{a_B^4e^4E^8}-\frac{320\left(\sum_k E_k^2\langle x_k^2\rangle\right)^9}{a_B^6e^6E^{12}}\right], \tag{5}$$

where $a_B=\hbar^2/me^2$ denotes the Bohr radius.

The electronic dipole moment $\mathbf{p}^{\mathrm{e}}$ of the core-shell system described by the wave function ψ is expressed as

$$\mathbf{p}^{\mathrm{e}}=\frac{(-e)\int\psi^*\mathbf{R}\psi\,dv}{\int\psi^*\psi\,dv}. \tag{6}$$

The component of $\mathbf{p}^{\mathrm{e}}$ along the l direction $(l=1,2,3)$ is written as

$$p_l^{\mathrm{e}}=\frac{(-e)\int\psi^*(\lambda)x_l\psi(\lambda)dv}{\int\psi^*(\lambda)\psi(\lambda)dv}=\frac{-2e\lambda E_l\langle x_l^2\rangle}{1+\lambda^2\sum_l E_l^2\langle x_l^2\rangle}. \tag{7}$$

Inserting λ from Eq. (5) into the last equation, and expanding into terms of $(\Sigma_k E_k^2\langle x_k^2\rangle)^3/(a_B^2e^2E^4)$ which are much smaller than unity (this assumption can be justified by using the values of the local electric field reported in Table IV), we obtain

$$p_l^{\mathrm{e}}=\frac{4}{a_B}\frac{\sum_k E_k^2\langle x_k^2\rangle}{E^2}\left[1-\frac{8E^2}{a_B^2e^2}\left(\frac{\sum_k E_k^2\langle x_k^2\rangle}{E^2}\right)^3+\frac{96E^4}{a_B^4e^4}\left(\frac{\sum_k E_k^2\langle x_k^2\rangle}{E^2}\right)^6-\frac{576E^6}{a_B^6e^6}\left(\frac{\sum_k E_k^2\langle x_k^2\rangle}{E^2}\right)^9\right]\times\langle x_l^2\rangle E_l. \tag{8}$$

In a coordinate system in which the component of the local electric field in the three-direction is dominating all other components, we have

$$\frac{\sum_k E_k^2\langle x_k^2\rangle}{E^2}\cong\langle x_3^2\rangle. \tag{9}$$

Then, the electronic dipole moment $\mathbf{p}_l^{\mathrm{e}}$ along the l direction becomes

$$p_l^{\mathrm{e}}\cong\frac{4\langle x_3^2\rangle\langle x_l^2\rangle}{a_B}\left[1-\frac{8\langle x_3^2\rangle^3}{a_B^2e^2}E^2+\frac{96\langle x_3^2\rangle^6}{a_B^4e^4}E^4-\frac{576\langle x_3^2\rangle^9}{a_B^6e^6}E^6\right]E_l. \tag{10}$$

The (k,l) element of the electronic polarizability tensor and the (k,l,l') element of the electronic hyperpolarizability tensor, respectively, are determined as follows:[22]

$$\alpha_{kl}=\frac{\partial p_k}{\partial E_l},\qquad \beta_{kll'}=\frac{\partial^2 p_k}{\partial E_l\partial E_{l'}}. \tag{11}$$

Following Eq. (10), α_{kl} and $\beta_{kll'}$ may be expressed for any orbital r as

$$\alpha_{kl,r}=\alpha_{k,r}^*[\delta_{kl}-\theta_r^*(E^2\delta_{kl}+2E_kE_l)+\xi_r^*(E^4\delta_{kl}+4E^2E_kE_l)-\zeta_r^*(E^6\delta_{kl}+6E^4E_kE_l)], \tag{12}$$

$$\beta_{kll',r}=\alpha_{k,r}^*(-2\theta_r^*+4\xi_r^*E^2-6\zeta_r^*E^4)(E_k\delta_{ll'}+E_l\delta_{kl'}+E_{l'}\delta_{kl}), \tag{13}$$

where

$$\alpha_{k,r}^*=\frac{4\langle x_3^2\rangle_r\langle x_k^2\rangle_r}{a_B}, \tag{14}$$

$$\theta_r^*=\frac{8\langle x_3^2\rangle_r^3}{a_B^2e^2}, \tag{15}$$

$$\xi_r^*=\frac{96\langle x_3^2\rangle_r^6}{a_B^4e^4}, \tag{16}$$

$$\zeta_r^* = \frac{576\langle x_3^2\rangle_r^9}{a_B^6 e^6}. \tag{17}$$

In Eqs. (12) and (13), δ_{kl} represents the Kronecker symbol. We assume the electronic polarizability and electronic hyperpolarizability of a considered j ion to result from summing over all contributions of respective orbitals namely, which means

$$\alpha_{kl}(j) = \sum_r \alpha_{kl,r}(j), \tag{18}$$

$$\beta_{kll'}(j) = \sum_r \beta_{kll',r}(j). \tag{19}$$

Equations (18) and (19) can be rearranged into

$$\begin{aligned}\alpha_{kl}(j) = \alpha_k^*(j)\{\delta_{kl} - \theta_k(j)[E^2(j)\delta_{kl} + 2E_k(j)E_l(j)] \\ + \xi_k(j)[E^4(j)\delta_{kl} + 4E^2(j)E_k(j)E_l(j)] \\ - \zeta_k(j)[E^6(j)\delta_{kl} + 6E^4(j)E_k(j)E_l(j)]\},\end{aligned} \tag{20}$$

$$\begin{aligned}\beta_{kll'}(j) = \alpha_k^*(j)[-2\theta_k(j) + 4\xi_k(j)E^2(j) - 6\zeta_k(j)E^4(j)] \\ \times[E_k(j)\delta_{ll'} + E_l(j)\delta_{kl'} + E_{l'}(j)\delta_{kl}],\end{aligned} \tag{21}$$

where

$$\alpha_k^*(j) = \sum_r \alpha_{k,r}^*(j), \tag{22}$$

$$\theta_k(j) = \frac{\sum_r \alpha_{k,r}^*(j)\theta_r^*(j)}{\sum_r \alpha_{k,r}^*(j)}, \tag{23}$$

$$\xi_k(j) = \frac{\sum_r \alpha_{k,r}^*(j)\xi_r^*(j)}{\sum_r \alpha_{k,r}^*(j)}, \tag{24}$$

$$\zeta_k(j) = \frac{\sum_r \alpha_{k,r}^*(j)\zeta_r^*(j)}{\sum_r \alpha_{k,r}^*(j)}. \tag{25}$$

For the calculation of the electronic polarizabilities and electronic hyperpolarizabilities of the Li$^+$, Nb^{5+}, and O^{2-} ions, we have used the Slater-type orbitals (see Ref. 16 for more detail),

$$\psi_{nlm} = \mathrm{Re}_{nl}(R)Y_{lm}(\Theta,\Phi), \tag{26}$$

where n, l, and m represent the principal, azimutal, and magnetic quantum numbers, R, Θ, and Φ are the spherical coordinates, and $\mathrm{Re}_{nl}(R)$ and $Y_{lm}(\Theta,\Phi)$ represent the radial part of the wave function and the spherical harmonics.

TABLE I. The fitted values of the effective charges of the outer layers of the constituent ions of LiNbO$_3$.

j ion	Effective	Charges
Li$^+$	$Z_{1s}^{(x)} = Z_{1s}^{(y)} = 2.5286$	$Z_{1s}^{(z)} = 2.5286$
Nb^{5+}	$Z_{3d,4sp}^{(x)} = Z_{3d,4sp}^{(y)} = 20.3144$	$Z_{3d,4sp}^{(z)} = 24.3472$
O^{2-}	$Z_{2sp}^{(x)} = Z_{2sp}^{(y)} = 3.4990$	$Z_{2sp}^{(z)} = 4.1535$

In order to calculate the coefficients $\theta_k(j)$, $\xi_k(j)$, and $\zeta_k(j)$ of a given j ion, we have used an anisotropic effective charge for the outer electronic layer of each ion. We then fit its components in such a way that the calculated values of the free electronic polarizabilities $\alpha_1^*(j)$, $\alpha_2^*(j)$, and $\alpha_3^*(j)$ coincide with the measured value of the free electronic polarizability $\alpha^{\mathrm{exp}}(j)$ of the same ion. The free electronic polarizabilities are calculated for $\mathbf{E}=0$. The effective charges of the other layers are determined by the Slater rules.[23] The fitted values are reported in Table I, while the values of the measured $\alpha^{\mathrm{exp}}(j)$ and the calculated $\theta_k(j)$, $\xi_k(j)$, and $\zeta_k(j)$ are reported in Table II.

Finally, the elements of the electronic polarizability and electronic hyperpolarizability tensor of the j ion, which will be used in the next section, are deduced from Table II and the following two relations:

$$\begin{aligned}\alpha_{kl}(j) = \alpha^{\mathrm{exp}}(j)\{\delta_{kl} - \theta_k(j)[E^2(j)\delta_{kl} + 2E_k(j)E_l(j)] + \xi_k(j) \\ \times[E^4(j)\delta_{kl} + 4E^2(j)E_k(j)E_l(j)] - \zeta_k(j)[E^6(j)\delta_{kl} \\ + 6E^4(j)E_k(j)E_l(j)]\},\end{aligned} \tag{27}$$

$$\begin{aligned}\beta_{kll'}(j) = \alpha^{\mathrm{exp}}(j)[-2\theta_k(j) + 4\xi_k(j)E^2(j) - 6\zeta_k(j)E^4(j)] \\ \times[E_k(j)\delta_{ll'} + E_l(j)\delta_{kl'} + E_{l'}(j)\delta_{kl}].\end{aligned} \tag{28}$$

By analyzing the results in Table II it appears that the oxygen which has the highest value of the free electronic polarizability α^{exp} has also the highest values of the coefficients θ_k, ξ_k, and ζ_k, particularly those in the three-direction which are almost twice as large as those obtained along the one- and two-direction. This means that, compared to all other ions, the electronic polarizability and electronic hyperpolarizability of the oxygen ions are affected much more, particularly in the three-direction.

Note that in the following section, the local electric field $\mathbf{E}$ will be rewritten as $\mathbf{E}^{\mathrm{loc}}$.

B. Dipole-dipole interaction

As mentioned above, our model is based on the dipole-dipole interaction in correlation with the quantum-mechanical orbital approximation. The model therefore accounts for the possible anisotropy in the electronic polarizability and electronic hyperpolarizability, the crystalline deformations, as well as the ionic shifts in the bulk.

The latter are of uttermost importance when modeling the ferroelectric system. To describe the geometry of LiNbO$_3$, one can either use the primitive rhombohedral unit cell with ten ions or the conventional hexagonal unit cell containing 30 ions[26] (which was used in this work. The ionic positions

TABLE II. The measured free electronic polarizabilities $\alpha^{\rm exp}$ (in Å^3) and the calculated values of the coefficients θ_k, ξ_k, and ζ_k (in esu CGS units) of the constituent ions of LiNbO$_3$.

j ion	Li$^+$	Nb^{5+}	O^{2-}
$\alpha^{\rm exp}(j)$	0.029 [a]	0.1859 [b]	1.976 [c]
$\theta_1(j)$	1.0418×10^{-16}	1.5818×10^{-16}	1.1462×10^{-14}
$\theta_2(j)$	1.0418×10^{-16}	1.5818×10^{-16}	1.1462×10^{-14}
$\theta_3(j)$	1.0418×10^{-16}	2.8812×10^{-16}	2.1434×10^{-14}
$\xi_1(j)$	1.6279×10^{-32}	1.0967×10^{-31}	4.5290×10^{-28}
$\xi_2(j)$	1.6279×10^{-32}	1.0967×10^{-31}	4.5290×10^{-28}
$\xi_3(j)$	1.6279×10^{-32}	2.2456×10^{-31}	9.4581×10^{-28}
$\zeta_1(j)$	1.2719×10^{-48}	4.4682×10^{-47}	1.0257×10^{-41}
$\zeta_2(j)$	1.2719×10^{-48}	4.4682×10^{-47}	1.0257×10^{-41}
$\zeta_3(j)$	1.2719×10^{-48}	9.3020×10^{-47}	2.1768×10^{-41}

[a] Reference 24.

[b] Reference 16.

[c] The value of $\alpha^{\rm exp}$ of the O^{2-} ion used here is the same as adopted in Refs. 18 and 21. This value is different from that used in the case of BaTiO$_3$ and KNbO$_3$ (which was 2.394 Å^3) (Refs. 16 and 15) because the electronic polarizability of the oxygen ion is very sensitive to the surrounding environment as stated by Kirsch (Ref. 25).

in the hexagonal unit cell are reported in Table IV). We therefore write the strains parallel to the hexagonal [100], [010], and [001] directions as Δ_1, Δ_2, and Δ_3, while the shearing concerning the (100), (010), and (001) planes are zero. The distance $\mathbf{r}(i,j)$ between the i and j ions in the ferroelectric ($R3c$) phase follows as

$$\mathbf{r}(i,j)=\begin{pmatrix}1+\Delta_1 & 0 & 0\\ 0 & 1+\Delta_2 & 0\\ 0 & 0 & 1+\Delta_3\end{pmatrix}\mathbf{r}(i,j)^0+[\mathbf{s}(j)-\mathbf{s}(i)], \tag{29}$$

with $\mathbf{r}(i,j)^0$ representing the interionic distance between i and j ion in the paraelectric ($R\overline{3}c$) phase, and $\mathbf{s}(i)$ and $\mathbf{s}(j)$ denoting the shifts of the i and j ions, respectively.

The unit-cell volume v then becomes

$$v=a_0^2c_0\sin\frac{\pi}{3}(1+\Delta_1)(1+\Delta_2)(1+\Delta_3), \tag{30}$$

where a_0 and c_0 denote the lattice constants in the paraelectric phase.

The distances $\mathbf{r}(i,j)$ and $\mathbf{r}(i,j)^0$ are expressed in the crystallographic coordinate system ($\mathbb{B}_{\rm g}$) having base vectors parallel to the crystallographic axes of the hexagonal system considered, which obviously are not orthogonal to each other. Knowing that the calculations rather should be performed in an orthonormal coordinate system, we then take the crystallophysic coordinate system ($\mathbb{B}_{\rm p}$) as the coordinate system for this aim being built up by the following three orthogonal base vectors: $\mathbf{x}_{\rm p}=[\cos(\pi/12),\sin(\pi/12),0]_{\mathbb{B}_{\rm g}}$, $\mathbf{y}_{\rm p}=[\sin(\pi/12),\cos(\pi/12),0]_{\mathbb{B}_{\rm g}}$, and $\mathbf{z}_{\rm p}=(0,0,1)_{\mathbb{B}_{\rm g}}$.

The local field acting on the i-ion along the k direction is expressed as[27]

$$E_k^{\rm loc}(i)=E_k^{\rm ext}+\sum_{j=1}^{30}\left(\sum_{k'=1}^{3}\sum_{\tilde{m}}\frac{3r_{k'}(i,j)r_k(i,j)-\delta_{kk'}r^2(i,j)}{\|\mathbf{r}(i,j)\|^5}p_{k'}(i,j)+\frac{4\pi}{3v}p_k(i,j)\right). \tag{31}$$

In the last equation, $\mathbf{E}^{\rm ext}$ represents an external electric field which generally is $\mathbf{E}^{\rm ext}=\mathbf{E}^{\rm bias}+\mathbf{E}^{\rm opt}$, with $\mathbf{E}^{\rm bias}$ the bias electric field, and $\mathbf{E}^{\rm opt}$ the optical electric field acting on the system. $\tilde{m}(m_x,m_y,m_z)$ represents the coordinates of a unit cell in the whole lattice, $\delta_{kk'}$ denotes the Kronecker symbol, and $p_{k'}(i,j)$ the dipole moment along the k' direction, which can be expressed as

$$p_{k'}(i,j)=p_{k'}^{\rm e}(j)+p_{k'}^{\rm i}(i,j), \tag{32}$$

with the two contributions $p_{k'}^{\rm e}(j)$ and $p_{k'}^{\rm i}(i,j)$ specifying the electronic dipole moment and the relative ionic dipole moment in the k'-direction of the j-ion as seen by the i-ion, respectively. These dipole moments are calculated as

$$p^{\mathrm{e}}_{k'}(j)=\sum_{l=1}^{3}\alpha_{k'l}(j)E_l^{\mathrm{loc}}(j)+\sum_{l=1}^{3}\sum_{l'=1}^{3}\beta_{k'll'}(j)E_l^{\mathrm{loc}}(j)E_{l'}^{\mathrm{loc}}(j), \tag{33}$$

and

$$p^{\mathrm{i}}_{k'}(i,j)=Z^{*}_{k'}(j)e[s_{k'}(j)-s_{k'}(i)]. \tag{34}$$

In Eq. (33), $\alpha_{k'l}(j)$ and $\beta_{k'll'}(j)$ represent, respectively, the $(k'l)$ element of the electronic polarizability tensor and the $(k'll')$ element of the electronic hyperpolarizability tensor of the j ion, given by Eqs. (27) and (28). In Eq. (34), $Z^{*}_{k'}(j)$ denotes the effective ionic charge along the k' direction of the j ion. Thus the local field present along the k direction acting on ion i can be written as

$$\sum_{j=1}^{30}\sum_{l=1}^{3}S_{kl}(i,j)E_l^{\mathrm{loc}}(j)=Q_k(i), \tag{35}$$

with

$$S_{kl}(i,j)=\delta_{kl}\delta_{ij}-\sum_{k'=1}^{3}T_{kk'}(i,j)(\alpha_{k'l}(j)+\sigma_{k'l}(j)), \tag{36}$$

and

$$Q_k(i)=E_k^{\mathrm{ext}}+\sum_{j=1}^{30}\sum_{k'=1}^{3}T_{kk'}(i,j)p^{\mathrm{i}}_{k'}(i,j), \tag{37}$$

where

$$T_{kk'}(i,j)=\sum_{\tilde{m}}\frac{3r_{k'}(i,j)r_k(i,j)-\delta_{kk'}r^2(i,j)}{\|\mathbf{r}(i,j)\|^5}+\frac{4\pi}{3v}\delta_{kk'}, \tag{38}$$

and

$$\sigma_{k'l}(j)=\sum_{l'=1}^{3}\beta_{k'll'}(j)E_{l'}^{\mathrm{loc}}(j). \tag{39}$$

The second-rank tensor $\tilde{\sigma}(j)$ is introduced in order to represent the effect of the electronic hyperpolarizability $\tilde{\beta}(j)$ tensor (third-rank tensor). In fact, such a procedure is adequate in order to avoid the difficulty encountered when transposing the third-rank $\tilde{\beta}(j)$ tensor from the coordinate system $\mathbb{B}_{\mathrm{q}}(j)$ (in which it is calculated: see Sec. III) into the coordinate system $\mathbb{B}_{\mathrm{p}}$ (in which it should be used).

From Eqs. (35) and (36) it appears that the components of the local electric field depend on those of the electronic polarizability and electronic hyperpolarizability, while these, in turn, depend on the electric field components through Eqs. (27) and (28). This mutual dependence, between electronic polarizability and electronic hyperpolarizability (orbital approximation) on one hand, and their dependence on the electric field (dipole-dipole interaction) on the other hand, makes a self-consistent calculation necessary.

By solving Eq. (35) we obtain $E_l^{\mathrm{loc}}(j)$, the (l,j) component of the local electric field. The total polarization P_k is expressed as

$$P_k=\frac{1}{v}\sum_{j=1}^{30}[p^{\mathrm{e}}_k(j)+p^{\mathrm{ion}}_k(j)], \tag{40}$$

with

$$p^{\mathrm{ion}}_k(j)=Z^{*}_k(j)es_k(j) \tag{41}$$

representing the absolute ionic dipole moment in the k direction of the j ion.

The connection between the optical dielectric constant $\varepsilon^{\mathrm{opt}}_{kl'}$, polarization P_k, and the optical electric field $E^{\mathrm{opt}}_{l'}$ is expressed in the following way:

$$\varepsilon^{\mathrm{opt}}_{kl'}=\delta_{kl'}+4\pi\frac{\partial P_k}{\partial E^{\mathrm{opt}}_{l'}}. \tag{42}$$

Here we have

$$\frac{\partial P_k}{\partial E^{\mathrm{opt}}_{l'}}=\frac{1}{v}\sum_{j=1}^{30}\frac{\partial p_k(j)}{\partial E^{\mathrm{opt}}_{l'}}. \tag{43}$$

By using Eq. (33), the term $\partial p_k(j)/\partial E^{\mathrm{opt}}_{l'}$ can be written as

$$\frac{\partial p_k(j)}{\partial E^{\mathrm{opt}}_{l'}}=\sum_{l=1}^{3}[\alpha_{kl}(j)+2\sigma_{kl}(j)]\frac{\partial E_l^{\mathrm{loc}}(j)}{\partial E^{\mathrm{opt}}_{l'}}. \tag{44}$$

Note that $\partial E_l^{\mathrm{loc}}(j)/\partial E^{\mathrm{opt}}_{l'}$ which represents the local electric field induced along the l direction of the j ion by unit of the l' component of optical electric field, can be obtained by solving the following equation, deduced from Eq. (31):

$$\sum_{j=1}^{30}\sum_{l=1}^{3}S^{*}_{kl}(i,j)\frac{\partial E_l^{\mathrm{loc}}(j)}{\partial E^{\mathrm{opt}}_{l'}}=\delta_{kl'}, \tag{45}$$

where

$$S^{*}_{kl}(i,j)=\delta_{kl}\delta_{ij}-\sum_{k'=1}^{3}T_{kk'}(i,j)[\alpha_{k'l}(j)+2\sigma_{k'l}(j)]. \tag{46}$$

In electromagnetic theory,[28] the index ellipsoid (also called optical indicatrix) in a given coordinate system may be written as

$$\sum_{k=1}^{3}\sum_{l=1}^{3}\eta^{\mathrm{opt}}_{kl}x_kx_l=1, \tag{47}$$

where η^{opt} represents the optical dielectric impermeability tensor of the medium $\tilde{\eta}^{\mathrm{opt}}=(\tilde{\varepsilon}^{\mathrm{opt}})^{-1}$, and x_1,x_2,x_3 are the coordinates of an arbitrary point M of the ellipsoid in the coordinate system. In this case the refractive index of the light polarized in the OM direction (O is the center of the

TABLE III. Numerical data of $LiNbO_3$ at room temperature: Lattice constants $a=a_0(1+\Delta_1)$ and $c=c_0(1+\Delta_3)$ (in Å), spontaneous ionic shifts (in Å), and effective ionic charges $Z^*_{k=1,2,3}(j)$ (in number of electrons). a_0 and c_0 are the lattice constants in the paraelectric phase.

Parameter	Value	Parameter	Value
a_0	5.2898[a]	c_0	13.8485[a]
a	5.1483[b]	c	13.8631[b]
$s_3(Li^+)$	0.51[b]	$Z^*_k(Li^+)$	0.64[c]
$s_3(Nb^{5+})$	0.06[b]	$Z^*_k(Nb^{5+})$	2.96[c]
$s_3(O^{2-})$	−0.20[b]	$Z^*_k(O^{2-})$	−1.20[c]

[a] Reference 29.
[b] Reference 2.
[c] Reference 18.

ellipsoid) is $n=\sqrt{(x_1^2+x_2^2+x_3^2)}$. In the special case of light being polarized along the k direction, the refractive index thus becomes

$$n_k=\frac{1}{\sqrt{\eta^{\mathrm{opt}}_{kk}}}. \tag{48}$$

III. RESULTS AND DISCUSSION

The calculation of the spontaneous polarization and refractive indices is carried out for $LiNbO_3$ at room temperature by using the data of lattice parameters, spontaneous ionic shifts, and effective ionic charges reported in Table III.

The calculation of the spontaneous local field $\mathbf{E}^{\mathrm{spon}}(j)$, which corresponds to the value of the local electric field $\mathbf{E}^{\mathrm{loc}}(j)$ of the j ion in the absence of any external electric field ($\mathbf{E}^{\mathrm{ext}}=0$), shows that this spontaneous local electric field of the O ions is not aligned along the three-direction in the crystallophysic coordinate system $\mathbb{B}_\mathrm{p}$. This means that the approximation in Eq. (9) is violated in $\mathbb{B}_\mathrm{p}$. To remedy the situation, we construct for each ion an own coordinate system $\mathbb{B}_\mathrm{q}(j)$ for which the z_q axis is parallel to the spontaneous local electric field of this ion (see Appendix B). The electronic polarizability and electronic hyperpolarizability are then calculated in this coordinate system, and afterwards transposed into the coordinate system $\mathbb{B}_\mathrm{p}$ in which the calculation of all other magnitudes is performed. In fact, the local field of a j ion is calculated in $\mathbb{B}_\mathrm{p}$ and then transposed to $\mathbb{B}_\mathrm{q}(j)$ in order to use it in the calculation of the tensors $\tilde{\alpha}(j)$ and $\tilde{\sigma}(j)$ of this ion. Once these tensors are calculated, we transpose them back to $\mathbb{B}_\mathrm{p}$ where they will be used in the calculation of all other magnitudes.

Note that the angles θ and φ, characterizing the $\mathbf{z}_\mathrm{q}$ vector of $\mathbb{B}_\mathrm{q}(j)$ relative to the j ion (see Fig. 1), can be evaluated as follows:

(i) If $\|\mathbf{E}^{\mathrm{loc}}(j)\|=0$ or $\sqrt{[E_1^{\mathrm{loc}}(j)]^2+[E_2^{\mathrm{loc}}(j)]^2}=0$:

$$\begin{cases}\theta(j)=0\\ \varphi(j)=0.\end{cases} \tag{49}$$

(ii) If $E_2^{\mathrm{loc}}(j)\geqslant 0$:

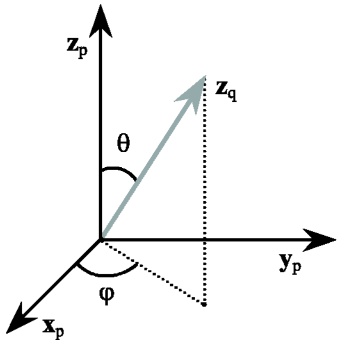

FIG. 1. Orientation of the z_q axis of the $\mathbb{B}_\mathrm{q}$ coordinate system within the $\mathbb{B}_\mathrm{p}$ coordinate system.

$$\begin{cases}\theta(j)=\arccos\dfrac{E_3^{\mathrm{loc}}(j)}{\|\mathbf{E}^{\mathrm{loc}}(j)\|}\\[2ex] \varphi(j)=\arccos\dfrac{E_1^{\mathrm{loc}}(j)}{\sqrt{[E_1^{\mathrm{loc}}(j)]^2+[E_2^{\mathrm{loc}}(j)]^2}}.\end{cases} \tag{50}$$

(iii) If $E_2^{\mathrm{loc}}(j)<0$:

$$\begin{cases}\theta(j)=\arccos\dfrac{E_3^{\mathrm{loc}}(j)}{\|\mathbf{E}^{\mathrm{loc}}(j)\|}\\[2ex] \varphi(j)=2\pi-\arccos\dfrac{E_1^{\mathrm{loc}}(j)}{\sqrt{[E_1^{\mathrm{loc}}(j)]^2+[E_2^{\mathrm{loc}}(j)]^2}}.\end{cases} \tag{51}$$

From the above relations, it seems that the angles θ and φ depend on the components of the local electric field which mutually depend on the component of both electronic polarizability and electronic hyperpolarizability. These last two magnitudes are calculated in the $\mathbb{B}_\mathrm{q}$ coordinate system, and then they depend on the values of θ and φ. This implicitly means that there exists a mutual dependence between the angles θ and φ on one hand, and the components of the local electric field on the other hand. Thus an imbricated doubly self-consistent calculation has to be performed.

The calculated values of the components of the spontaneous local electric field acting on the constituent ions of $LiNbO_3$ with those of the angles θ and φ are reported in Table IV. Note that the results shown here are expressed in the $\mathbb{B}_\mathrm{p}$ coordinate system.

The results in Table IV illustrate that all ions of the same type have the same amplitude of spontaneous local electric field. However, the spontaneous local electric fields for Li^+ and Nb^{5+} ions are parallel to the polar axis (i.e., z axis), while the O^{2-} ions have different orientations of their spontaneous local electric fields. They are all inclined by an angle $\theta=32.50°$ to the polar axis, while the angle φ is different for every ion. It is noteworthy that the ions numbered in Table IV from $j=11$ to 20 and from $j=21$ to 30, have the same local electric field [$\mathbf{E}^{\mathrm{spon}}(j+10)=\mathbf{E}^{\mathrm{spon}}(j+20)=\mathbf{E}^{\mathrm{spon}}(j)$; j changes from 1 to 10].

The elements of the electronic polarizability tensor $\tilde{\alpha}(j)$ of the j ion in the spontaneous state ($\mathbf{E}^{\mathrm{ext}}=0$) are evaluated by considering Eq. (27) and Tables II and IV. The calculated

TABLE IV. Calculated values of the components of the spontaneous local electric field and the angles θ and φ (in degrees) characterizing the orientation of the spontaneous local electric field of the constituent ions of $LiNbO_3$ at room temperature.

j ion	Type	Position	$E_1^{\text{spon}}(j)$	$E_2^{\text{spon}}(j)$	$E_3^{\text{spon}}(j)$	$\lVert\mathbf{E}^{\text{spon}}(j)\rVert$	$\theta(j)$	$\varphi(j)$
1	Li^+	$(0\ 0\ 0)$	0	0	0.8673	0.8673	0	0
2	O^{2-}	$(\frac{1}{3}\ 0\ 0)$	-0.2849	0.8630	1.4268	1.6917	32.50	108.27
3	O^{2-}	$(0\ \frac{1}{3}\ 0)$	-0.6049	-0.6783	1.4268	1.6917	32.50	228.27
4	O^{2-}	$(\frac{2}{3}\ \frac{2}{3}\ 0)$	0.8898	-0.1848	1.4268	1.6917	32.50	348.27
5	Nb^{5+}	$(\frac{2}{3}\ \frac{1}{3}\ \frac{1}{12})$	0	0	2.0175	2.0175	0	0
6	Li^+	$(\frac{1}{3}\ \frac{2}{3}\ \frac{2}{12})$	0	0	0.8673	0.8673	0	0
7	O^{2-}	$(\frac{2}{3}\ 0\ \frac{2}{12})$	0.1848	-0.8898	1.4268	1.6917	32.50	281.73
8	O^{2-}	$(\frac{1}{3}\ \frac{1}{3}\ \frac{2}{12})$	-0.8630	0.2849	1.4268	1.6917	32.50	161.73
9	O^{2-}	$(0\ \frac{2}{3}\ \frac{2}{12})$	0.6783	0.6049	1.4268	1.6917	32.50	41.73
10	Nb^{5+}	$(0\ 0\ \frac{3}{12})$	0	0	2.0175	2.0175	0	0
11	Li^+	$(\frac{2}{3}\ \frac{1}{3}\ \frac{4}{12})$	0	0	0.8673	0.8673	0	0
12	O^{2-}	$(0\ \frac{1}{3}\ \frac{4}{12})$	-0.2849	0.8630	1.4268	1.6917	32.50	108.27
13	O^{2-}	$(\frac{2}{3}\ \frac{2}{3}\ \frac{4}{12})$	-0.6049	-0.6783	1.4268	1.6917	32.50	228.27
14	O^{2-}	$(\frac{1}{3}\ 0\ \frac{4}{12})$	0.8899	-0.1848	1.4268	1.6917	32.50	348.27
15	Nb^{5+}	$(\frac{1}{3}\ \frac{2}{3}\ \frac{5}{12})$	0	0	2.0175	2.0175	0	0
16	Li^+	$(0\ 0\ \frac{6}{12})$	0	0	0.8673	0.8673	0	0
17	O^{2-}	$(\frac{1}{3}\ \frac{1}{3}\ \frac{6}{12})$	0.1848	-0.8899	1.4268	1.6917	32.50	281.73
18	O^{2-}	$(0\ \frac{2}{3}\ \frac{6}{12})$	-0.8630	0.2849	1.4268	1.6917	32.50	161.73
19	O^{2-}	$(\frac{2}{3}\ 0\ \frac{6}{12})$	0.6783	0.6049	1.4268	1.6917	32.50	41.73
20	Nb^{5+}	$(\frac{2}{3}\ \frac{1}{3}\ \frac{7}{12})$	0	0	2.0175	2.0175	0	0
21	Li^+	$(\frac{1}{3}\ \frac{2}{3}\ \frac{8}{12})$	0	0	0.8673	0.8673	0	0
22	O^{2-}	$(\frac{2}{3}\ \frac{2}{3}\ \frac{8}{12})$	-0.2849	0.8630	1.4268	1.6917	32.50	108.27
23	O^{2-}	$(\frac{1}{3}\ 0\ \frac{8}{12})$	-0.6049	-0.6783	1.4268	1.6917	32.50	228.27
24	O^{2-}	$(0\ \frac{1}{3}\ \frac{8}{12})$	0.8898	-0.1848	1.4268	1.6917	32.50	348.27
25	Nb^{5+}	$(0\ 0\ \frac{9}{12})$	0	0	2.0175	2.0175	0	0
26	Li^+	$(\frac{2}{3}\ \frac{1}{3}\ \frac{10}{12})$	0	0	0.8673	0.8673	0	0
27	O^{2-}	$(0\ \frac{2}{3}\ \frac{10}{12})$	0.1848	-0.8898	1.4268	1.6917	32.50	281.73
28	O^{2-}	$(\frac{2}{3}\ 0\ \frac{10}{12})$	-0.8630	0.2849	1.4268	1.6917	32.50	161.73
29	O^{2-}	$(\frac{1}{3}\ \frac{1}{3}\ \frac{10}{12})$	0.6783	0.6049	1.4268	1.6917	32.50	41.73
30	Nb^{5+}	$(\frac{1}{3}\ \frac{2}{3}\ \frac{11}{12})$	0	0	2.0175	2.0175	0	0

values reported in Table V show that for the Li^+ and Nb^{5+} ions, the tensor $\tilde{\alpha}(j)$ is diagonal (i.e., only the diagonal elements are nonzero). For the O^{2-} ions, however, $\tilde{\alpha}(j)$ is symmetric nondiagonal although it appears to be diagonal in the $\mathbb{B}_q(j)$ coordinate system. Note that in Table V, we only illustrate results for ions numbered from $j=1$ to 10, because all other numbers are obtained from $\tilde{\alpha}(j+10)=\tilde{\alpha}(j+20)=\tilde{\alpha}(j)$.

The electronic polarizabilities of the O^{2-} ions show a remarkable anisotropy. However, comparing the diagonal elements, $\alpha_{33}(j)$ is the same for all oxygens, but smaller compared to $\alpha_{11}(j)$ and $\alpha_{22}(j)$, which change for all oxygens. The tensor $\tilde{\sigma}(j)$, which can be considered as an additional electronic polarizability besides the $\tilde{\alpha}(j)$ tensor, represents the effect of the electronic hyperpolarizability $\tilde{\beta}(j)$. The elements of this tensor, in the spontaneous state ($\mathbf{E}^{\text{ext}}=0$), are evaluated by considering Eqs. (28) and (39), and Tables II and IV. The analysis of the calculated values reported in Table VI show that, as for $\tilde{\alpha}(j)$, $\tilde{\sigma}(j)$ is symmetric nondiagonal for the O^{2-} ions. Also for the diagonal elements, the value of the element $\sigma_{33}(j)$, which is the same for all oxygens, is much smaller compared to $\sigma_{11}(j)$ and $\sigma_{22}(j)$, which again change for all oxygens.

The spontaneous polarization P^{spon} is defined as the total dipole moment by unit volume, with the components P_k being deduced from Eq. (40) in the absence of any external field. The calculation shows that only the three-component of the spontaneous polarization is nonzero, having the value of $P^{\text{spon}}=0.7219\ \text{C/m}^2$. This value is in good accordance with the experimentally measured value of $0.70\ \text{C/m}^2$ according to Xu,[2] or $0.75\ \text{C/m}^2$ according to Kim.[7]

TABLE V. Calculated values of the components of the electronic polarizability tensors $\tilde{\alpha}(j)$ (in Å^3) for the constituent ions of $LiNbO_3$ at room temperature.

j ion	$\alpha_{11}(j)$	$\alpha_{12}(j)$	$\alpha_{13}(j)$	$\alpha_{21}(j)$	$\alpha_{22}(j)$	$\alpha_{23}(j)$	$\alpha_{31}(j)$	$\alpha_{32}(j)$	$\alpha_{33}(j)$
1	0.0290	0	0	0	0.0290	0	0	0	0.0290
2	1.9113	0.0203	0.0336	0.0203	1.8566	−0.1016	0.0336	−0.1016	1.7500
3	1.8879	−0.0339	0.0712	−0.0339	1.8801	0.0799	0.0712	0.0799	1.7500
4	1.8527	0.0136	−0.1048	0.0136	1.9152	0.0218	−0.1048	0.0218	1.7500
5	0.1858	0	0	0	0.1858	0	0	0	0.1852
6	0.0290	0	0	0	0.0290	0	0	0	0.0290
7	1.9152	0.0136	−0.0218	0.0136	1.8527	0.1048	−0.0218	0.1048	1.7500
8	1.8566	0.0203	0.1016	0.0203	1.9113	−0.0336	0.1016	−0.0336	1.7500
9	1.8801	−0.0339	−0.0799	−0.0339	1.8878	−0.0712	−0.0799	−0.0712	1.7500
10	0.1858	0	0	0	0.1858	0	0	0	0.1852

Finally, the numbers for the ordinary and extraordinary refractive indices are calculated to $n_o = 2.2824$ and $n_e = 2.2282$. These values agree well with experimentally obtained values given in literature, which are[2,4] $n_o = 2.286$ and $n_e = 2.200$.

IV. CONCLUSIONS

By using a microscopic model taking into account a quantum method based upon the orbital approximation and the dipole-dipole interaction due to the local electric field acting on the constituent ions, we have studied the electrical and optical properties of $LiNbO_3$ at room temperature. The calculation shows that the experimental data of the spontaneous polarization and refractive indices is successfully explained by considering the nonlinearity and anisotropy of the electronic polarizability and electronic hyperpolarizability of the constituent ions, particularly that of the O^{2-} ions. Furthermore, we observe that, in contrast to tetragonal $BaTiO_3$,[14] the local electric field of the O^{2-} ions in $LiNbO_3$ is not aligned parallel to the direction of spontaneous polarization.

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APPENDIX A: DETERMINATION OF THE VARIATIONAL PARAMETER λ

The energy I of the system can be written as

$$I = \frac{\int \psi^* H \psi dv}{\int \psi^* \psi dv} = \frac{I_0 + 2\lambda e \sum_k E_k^2 \langle x_k^2 \rangle + \lambda^2 \sum_k E_k^2 \langle x_k H_0 x_k \rangle}{1 + \lambda^2 \sum_k E_k^2 \langle x_k^2 \rangle}. \tag{A1}$$

The terms with odd powers of x_k are omitted because they are zero when the wave function ψ_0 is replaced by the real form of the wave function ψ_{nlm} used in this work [Eq. (26)]. This assumption can be justified by considering the parity of the real form of the wave functions, ψ_{nlm}, and that of the odd powers of x_k. In Eq. (A1), I_0 represents the energy in $\mathbf{E} = 0$. By assuming that the wave function is normalized to unity, namely $\langle \psi_0 | \psi_0 \rangle = 1$, I_0 can be expressed as

$$I_0 = \int \psi_0^* H_0 \psi_0 dv. \tag{A2}$$

TABLE VI. Calculated values of the components of the tensors $\tilde{\sigma}(j)$ (in Å^3) for the constituent ions of $LiNbO_3$ at room temperature.

j ion	$\sigma_{11}(j)$	$\sigma_{12}(j)$	$\sigma_{13}(j)$	$\sigma_{21}(j)$	$\sigma_{22}(j)$	$\sigma_{23}(j)$	$\sigma_{31}(j)$	$\sigma_{32}(j)$	$\sigma_{33}(j)$
1	0	0	0	0	0	0	0	0	0
2	−0.1134	0.0310	0.0512	0.0310	−0.1969	−0.1550	0.0512	−0.1550	−0.3595
3	−0.1492	−0.0517	0.1087	−0.0517	−0.1611	0.1218	0.1087	0.1218	−0.3595
4	−0.2029	0.0207	−0.1598	0.0207	−0.1075	0.0332	−0.1598	0.0332	−0.3595
5	−0.0002	0	0	0	−0.0002	0	0	0	−0.0013
6	0	0	0	0	0	0	0	0	0
7	−0.1075	0.0207	−0.0332	0.0207	−0.2029	0.1598	−0.0332	0.1598	−0.3595
8	−0.1969	0.0310	0.1550	0.0310	−0.1134	−0.0512	0.1550	−0.0512	−0.3595
9	−0.1611	−0.0517	−0.1218	−0.0517	−0.1492	−0.1087	−0.1218	−0.1087	−0.3595
10	−0.0002	0	0	0	−0.0002	0	0	0	−0.0013

In Eq. (A1), the index $k=1,2,3$ represents the directions x, y, and z. The terms $\langle x_k^2\rangle$ and $\langle x_kH_0x_k\rangle$ are written as

$$\langle x_k^2\rangle=\int \psi_0^* x_k^2\psi_0 dv, \tag{A3}$$

$$\langle x_kH_0x_k\rangle=\int \psi_0^* x_kH_0x_k\psi_0 dv. \tag{A4}$$

By using the variational principle, namely $\partial I/\partial\lambda=0$, we can calculate the value of λ and determine the wave function $\psi(\lambda)$ under the electric field by the condition

$$\frac{\partial I}{\partial\lambda}=0=\lambda^2 e\left(\sum_k E_k^2\langle x_k^2\rangle\right)^2+\lambda\left(I_0\sum_k E_k^2\langle x_k^2\rangle-\sum_k E_k^2\langle x_kH_0x_k\rangle\right)-e\sum_k E_k^2\langle x_k^2\rangle. \tag{A5}$$

In quantum mechanics, one shows that

$$\langle x_kH_0x_k\rangle=\langle x_k^2\rangle I_0+\frac{\hbar^2}{2m}. \tag{A6}$$

By using Eqs. (A5) and (A6), and replacing $\Sigma_kE_k^2$ by E^2, we get

$$\lambda=\frac{\frac{E^2\hbar^2}{2m}\pm\left[\frac{E^4\hbar^4}{4m^2}+4e^2\left(\sum_k E_k^2\langle x_k^2\rangle\right)^3\right]^{1/2}}{2e\left[\sum_k E_k^2\langle x_k^2\rangle\right]^2}. \tag{A7}$$

Under the condition of minimal energy, only the smaller solution of λ is meaningful in Eq. (A7). Expanding Eq. (A7) into terms including E_k^6, we directly obtain for λ:

$$\lambda=-\frac{2\sum_k E_k^2\langle x_k^2\rangle}{a_BeE^2}\left[1-\frac{4\left(\sum_k E_k^2\langle x_k^2\rangle\right)^3}{a_B^2e^2E^4}+\frac{32\left(\sum_k E_k^2\langle x_k^2\rangle\right)^6}{a_B^4e^4E^8}-\frac{320\left(\sum_k E_k^2\langle x_k^2\rangle\right)^9}{a_B^6e^6E^{12}}\right], \tag{A8}$$

where $a_B=\hbar^2/me^2$ is the Bohr radius.

APPENDIX B: CONSTRUCTION OF THE $\mathbb{B}_\mathrm{q}$ COORDINATE SYSTEM

The components of the unit vector $\mathbf{z}_\mathrm{q}$ of the coordinate system $\mathbb{B}_\mathrm{q}$, formed by the triplet $(\mathbf{x}_\mathrm{q},\mathbf{y}_\mathrm{q},\mathbf{z}_\mathrm{q})$, in the coordinate system $\mathbb{B}_\mathrm{p}$, formed by the triplet $(\mathbf{x}_\mathrm{p},\mathbf{y}_\mathrm{p},\mathbf{z}_\mathrm{p})$, are shown in Fig. 1:

$$\mathbf{z}_\mathrm{q}=\begin{pmatrix}\sin\theta\cos\varphi\\ \sin\theta\sin\varphi\\ \cos\theta\end{pmatrix}_{\mathbb{B}_\mathrm{p}}. \tag{B1}$$

$\mathbb{B}_\mathrm{q}$ forms a direct orthonormal basis. This can be summarized by

$$\begin{cases}\mathbf{x}_\mathrm{q}\cdot\mathbf{z}_\mathrm{q}=0\\ \mathbf{x}_\mathrm{q}\cdot\mathbf{x}_\mathrm{q}=1\\ \mathbf{y}_\mathrm{q}=\mathbf{z}_\mathrm{q}\wedge\mathbf{x}_\mathrm{q}.\end{cases} \tag{B2}$$

There is an infinite number of doublets $(\mathbf{x}_\mathrm{q},\mathbf{y}_\mathrm{q})$ which fulfil the above requirements, and all of them may be used in order to construct $\mathbb{B}_\mathrm{q}$. Here we have chosen a doublet for which $\mathbf{x}_\mathrm{q}\perp\mathbf{y}_\mathrm{p}$ (i.e., $\mathbf{x}_\mathrm{q}\cdot\mathbf{y}_\mathrm{p}=0$). By solving the above equalities we get

$$\mathbf{x}_\mathrm{q}=\begin{pmatrix}\frac{1}{\sqrt{1+\tan^2\theta\cos^2\varphi}}\\ 0\\ -\frac{\tan\theta\cos\varphi}{\sqrt{1+\tan^2\theta\cos^2\varphi}}\end{pmatrix}_{\mathbb{B}_\mathrm{p}}, \tag{B3}$$

$$\mathbf{y}_\mathrm{q}=\begin{pmatrix}-\frac{\sin\theta\sin\varphi\tan\theta\cos\varphi}{\sqrt{1+\tan^2\theta\cos^2\varphi}}\\ \frac{\cos\theta+\sin\theta\tan\theta\cos^2\varphi}{\sqrt{1+\tan^2\theta\cos^2\varphi}}\\ -\frac{\sin\theta\sin\varphi}{\sqrt{1+\tan^2\theta\cos^2\varphi}}\end{pmatrix}_{\mathbb{B}_\mathrm{p}}. \tag{B4}$$

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*Corresponding author. Electronic address: eng@iapp.de

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