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Density matrix and x-ray structure factors in LiH

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Within the first-order density-matrix formalism of Löwdin, we show how to obtain the density matrix in closed-shell crystals setting up the inverse of the overlap matrix between Bloch sums at a few selected $\vec{k}$ vectors. Overlap effects in x-ray structure factors in LiH are taken into account in the calculations avoiding to perform a spherical average of the charge density with regard to each nucleus. Using hydrogenic wave functions with optimized screening for LiH, we obtain structure amplitudes in better agreement with experiment than previous calculations.

I. INTRODUCTION

Since Hylleraas' pioneering work[1] on cohesive energy, solid lithium hydride has attracted considerable interest because of its simplicity from the point of view of the electronic structure. The very diffuse nature of hydride-ion wave functions gave in early theoretical works results conflicting with experiments and stimulated even more the investigations in LiH both for their intrinsic interest or/and as a test before considering more complicated crystals.

It is now well established that a proper account of overlap effects is essential in understanding physical properties of LiH. Lundqvist *et al.*[2] first pointed out the importance of overlap effects in calculation of cohesive energy of LiH. Berggren *et al.*[3] have shown that overlap effects are basic to bring Compton-profile calculations in agreement with experiments[4]; further theoretical and experimental investigations[5-7] have confirmed this fact. Overlap effects are also very important in determining crystal charge density and elastic x-ray scattering as demonstrated by Waller *et al.*[8] and by Kahane *et al.*[9]

In this paper, Sec. II, within the first-order density-matrix formalism of Löwdin,[10] we derive an efficient procedure for obtaining the density matrix in crystals composed by closed-shell units and we apply it to the case of LiH crystals. Our procedure, compared with previous *ad hoc* methods[2-5] developed for the specific case of LiH crystals and s-like wave functions, turns out to be quite simple and manageable basically because translational symmetry is fully exploited from the very beginning. In Sec. III we calculate the x-ray structure factors, which are primarily related to the crystal charge density. For this purpose we use a continuous Gaussian transform of Slater-type orbitals (STO) following the computational technique introduced by Lafon and Lin[11] in their work on band structure of lithium. With this technique we can avoid to perform a spherical average of the charge density with regard to each nucleus. Our results are then compared both with experiment of Calder *et al.*[12] and with previous calculations.[8,9]

II. DENSITY MATRIX IN CLOSED-SHELL CRYSTALS

A. Expression of density-matrix coefficients

The crystal structure of LiH is fcc with lattice constant[13] $a_0 = 7.720$ a.u. The fundamental vectors $\vec{\tau}_i$ and $\vec{g}_i$ of the direct and reciprocal lattice are given by $\vec{\tau}_1 = (a_0/2)(0,1,1)$, $\vec{g}_1 = (2\pi/a_0)(-1,1,1)$ and cyclic permutations, respectively. The unit cell has a basis with hydride and lithium ions in the positions $\vec{d}_1 = 0$ and $\vec{d}_2 = (a_0/2)(1,0,0)$.

Following most of the works in the literature, we adopt the ionic picture for LiH and assume the simple closed-shell electronic configuration Li$^+$ $1s^2$, H$^-$ $1s^2$, where $1s$ functions are STO's of the form $\phi(r) = (\alpha^3/\pi)^{1/2} e^{-\alpha r}$. For the numerical work the screening α_{Li} for Li$^+$ ions is set equal to the free ion value $\alpha_{Li} = 3 - \frac{5}{16} = 2.6875$ a.u. The screening α_H for hydride ions is taken $\alpha_H = 0.7724$, which is the optimized screening of an hydride ion in the point charge field for the rest of the lattice[14]; this screening leads to Compton profile[6,7] in close agreement with experiments.[7]

The problem of the explicit determination of density matrix in closed-shell crystals is not satisfactorily settled yet (for a review see, for instance, Refs. 6 and 15); usually one has to adopt the series expansion method of Löwdin[10] with truncation to second order even when off-diagonal terms in overlap matrix are not small enough to justify it; in the particular case of LiH crystals, in which there are only s states, *ad hoc* procedures have been developed.[2,3,5] We present now a workable procedure for obtaining the density matrix in any closed-shell crystal; the application to LiH crystals will show the practical convenience and simplicity.

According to a general result of Löwdin,[10] the spinless density matrix for crystals composed by closed-shell units (ions, atoms, or molecules) is given by

$$\rho(\vec{r},\vec{r}\,') = 2\sum_{\mu\nu}\sum_{\vec{\tau}_m\vec{\tau}_n} \phi^*_\mu(\vec{r}-\vec{d}_\mu-\vec{\tau}_m)T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n} \times\phi_\nu(\vec{r}\,'-\vec{d}_\nu-\vec{\tau}_n)\,, \tag{1}$$

where $\vec{\tau}_m$ and $\vec{\tau}_n$ are translation vectors, μ and ν label all occupied orbitals in the unit cell in the appropriate centers $\vec{d}_\mu$ and $\vec{d}_\nu$, matrix T is the inverse of the overlap matrix S, whose elements

$$S_{\mu\vec{\tau}_m,\nu\vec{\tau}_n} = \langle \phi_\mu(\vec{r}-\vec{d}_\mu-\vec{\tau}_m)\,|\,\phi_\nu(\vec{r}-\vec{d}_\nu-\vec{\tau}_n)\rangle\,, \tag{2}$$

are two-center integrals between atomic (or molecular) orbitals. The overlap integrals (2) can be expressed in terms of independent parameters[16] and computed with standard programs. The basic relation

$$\sum_{\nu\vec{\tau}_n} S_{\mu\vec{\tau}_m,\nu\vec{\tau}_n}\, T_{\nu\vec{\tau}_n,\mu'\vec{\tau}\,'_m} = \delta_{\mu\mu'}\,\delta_{\vec{\tau}_m\vec{\tau}\,'_m} \tag{3}$$

is known as the Löwdin theorem.[10]

Equation (3) determines in principle the matrix elements $T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n}$, but we provide here a more convenient expression for them starting from the standard Bloch sums

$$\Phi_\mu(\vec{k},\vec{r}) = \frac{1}{\sqrt{N_c}}\sum_{\vec{\tau}_m} e^{i\vec{k}\cdot\vec{\tau}_m}\,\phi_\mu(\vec{r}-\vec{d}_\mu-\vec{\tau}_m)\,, \tag{4}$$

where N_c is the number of unit cells of the crystal. At a generical $\vec{k}$ vector, we consider the overlap matrix $S(\vec{k})$ with elements

$$S_{\mu\nu}(\vec{k}) = \langle \Phi_\mu(\vec{k},\vec{r})\,|\,\Phi_\nu(\vec{k},\vec{r})\rangle\,, \tag{5}$$

and rank equal to the number of occupied orbitals. The matrix $S(\vec{k})$ can be easily inverted by standard programs because of its (usually) small rank and we indicate by $T(\vec{k})$ its inverse. At any $\vec{k}$ vector, the contribution to the crystal density matrix from the Bloch sums (4) is [regardless of the fact that the basis functions (4) are not normalized]

$$\rho_{\vec{k}}(\vec{r},\vec{r}\,') = 2\sum_{\mu\nu}\Phi^*_\mu(\vec{k},\vec{r})T_{\mu\nu}(\vec{k})\Phi_\nu(\vec{k},\vec{r}\,')\,. \tag{6}$$

Summing up this expression over $\vec{k}$ and using Eq. (4), we obtain Eq. (1) for the crystal density matrix with

$$T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n} = \frac{1}{N_c}\sum_{\vec{k}} T_{\mu\nu}(\vec{k})e^{-i\vec{k}\cdot(\vec{\tau}_m-\vec{\tau}_n)}\,. \tag{7}$$

Equation (7) shows that matrix elements $T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n}$ [which can be indicated at $T_{\mu\nu}(\vec{\tau})$ with $\vec{\tau}=\vec{\tau}_n-\vec{\tau}_m$] are the Fourier transforms in direct space of the matrix elements $T_{\mu\nu}(\vec{k})$, which are periodic functions in the reciprocal lattice. It is important to notice that Eq. (3) is automatically satisfied when elements $T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n}$ are given by Eq. (7), as it can be easily verified; Eq. (7) thus constitutes an important stage toward the explicit inversion of the overlap matrix (2).

B. Computation of density-matrix coefficients

The crucial point to compute the density-matrix coefficients $T_{\mu\nu}(\vec{\tau})$ is to perform the sum over $\vec{k}$ in Eq. (7). The problem of optimized choices of $\vec{k}$ vectors has been considered in the literature[17,18] and we discuss here the application to our specific problem.

Given a generical function $F(\vec{k})$ periodic in $\vec{k}$ space, consider first the sum over the Brillouin zone

$$S = \frac{1}{N_c}\sum_{\vec{k}}^{\text{BZ}} F(\vec{k})\,. \tag{8}$$

We can expand $F(\vec{k})$ in Fourier series with translation vectors $\vec{\tau}_n$,

$$F(\vec{k}) = \sum_{\vec{\tau}_n} F_n\, e^{i\vec{k}\cdot\vec{\tau}_n}\,, \tag{9}$$

and thus obtain

$$S = F_0\,. \tag{10}$$

As in Ref. 18, we consider the set of $N_1N_2N_3$ mesh points $\vec{k}_m$ defined by

$$\vec{k}_m = \frac{m_1}{N_1}\vec{g}_1 + \frac{m_2}{N_1}\vec{g}_2 + \frac{m_3}{N_3}\vec{g}_3\,, \quad 0 \leqslant m_i \leqslant N_i - 1\,, \tag{11}$$

where N_1, N_2, N_3 are arbitrary (and small) positive numbers. If we consider the sum over the mesh points (11),

$$S_{\text{mesh}} = \frac{1}{N_1N_2N_3}\sum_{\vec{k}_m}^{\text{mesh}} F(\vec{k}_m)\,, \tag{12}$$

we obtain

$$S_{\text{mesh}} = F_0 + \sum_{\vec{\tau}_N}{}' F_N\,, \tag{13}$$

where $\vec{\tau}_N$ is a generical vector of the "superlattice" with fundamental vectors $N_1\vec{\tau}_1, N_2\vec{\tau}_2, N_3\vec{\tau}_3$. Comparing Eq. (10) with Eq. (13), we see that S_{mesh} differs from the exact sum S because of the appearance of the Fourier coefficients F_N corresponding to the superlattice vectors $\vec{\tau}_N$. *If* *function* $F(\vec{k})$ *is reasonably smooth in* $\vec{k}$ *space, or equivalently if* $F(\vec{\tau})$ *is reasonably peaked in direct space* (and this is certainly true for the density matrix coefficients) we can replace with negligible errors Eq. (8) by Eq. (12).

The same reasoning can be applied to perform a sum of the type

$$S=\frac{1}{N_c}\sum_{\vec{k}} F(\vec{k})e^{i\vec{k}\cdot\vec{\tau}_n}\,; \tag{14}$$

if $\vec{\tau}_n=n_1\vec{\tau}_1+n_2\vec{\tau}_2+n_3\vec{\tau}_3$ has indices n_i much smaller than N_i, we can evaluate Eq. (14) using the mesh points (11).

In the specific case of LiH crystals, we have two Bloch sums corresponding to 1*s* STO's of Li$^+$ and H$^-$ ions. At a generical $\vec{k}$ vector, the 2×2 overlap matrix $S_{\mu\nu}(\vec{k})$ is inverted by hand and the sum over $\vec{k}$ to obtain $T_{\mu\nu}(\vec{\tau}_n)$ is performed on the mesh points (11) with $N_i=|n_i|+N$ and $N=5$, after testing the very good reliability of the results as N is varied and after comparison with the cluster inversion method of Ref. 6; this means that a mesh of about 125 points was more than sufficient for our case. The density-matrix coefficients $T_{\mu\nu}(\vec{\tau})$ are reported in Table I; $T_{\mu\nu}(\vec{\tau})$ have been neglected only for $|\vec{\tau}|$ larger than $|\vec{\tau}_1+\vec{\tau}_2+\vec{\tau}_3|$ $=\sqrt{12}\,(a_0/2)$, i.e., besides the 13th shell (13 shells include 179 ions), because a large number of neighbors is essential for this kind of crystal. To show in a more transparent way the simplification achieved with the above described procedure, let us suppose to neglect the overlap between Li$^+$ and H$^-$ wave functions; in this case we have, say, for the hydride-ions sublattice

$$T_{\mathrm{H\,H}}(\vec{k})=\frac{1}{\sum_\nu S_{0\nu}e^{i\vec{k}\cdot\vec{\tau}_\nu}}\;,$$

where the sum over ν extends in our calculations to the first 87 H$^-$ neighbor ions; using the relation $\vec{g}_i\cdot\vec{\tau}_j=2\pi\delta_{ij}$ and the mesh points (11) we obtain

$$T_{\mathrm{H\,H}}(\vec{\tau}_n)=\frac{1}{N_1N_2N_3}\sum_{m_1m_2m_3}^{0\cdots(N_i-1)}\frac{\cos 2\pi[m_1(n_1/N_1)+m_2(n_2/N_2)+m_3(n_3/N_3)]}{\sum_\nu S_{0\nu}\cos 2\pi[m_1(\nu_1/N_1)+m_2(\nu_2/N_2)+m_3(\nu_3/N_3)]}\;.$$

Only slightly more involved expressions have to be considered for taking into account Li and H$^-$ wave functions mixing, which is small but not negligible, as can be seen from Table I.

Before concluding this section, we note that in most closed-shell crystals (which include solid rare gases, alkali halides, several molecular crystals) the density-matrix coefficients are more localized in direct lattice and the number of mesh points (11) sufficient for their evaluation is expected to become smaller. Of course, one can exploit the symmetry operations of the crystal point group for a further reduction of the number of independent $\vec{k}$ vectors in the mesh (11). In non-closed-shell crystals or also in closed-shell crystals when other localized orbitals are added to the minimal basis set, the sum procedure of Sec. II B can again be applied but the coefficients $T_{\mu\nu}(\vec{k})$ appearing in Eq. (6) require a detailed band-structure calculation; $T_{\mu\nu}(\vec{k})$ can be obtained if the expansion coefficients of the occupied crystal states on the basis functions (4) are known.

III. X-RAY STRUCTURE FACTORS IN LiH

The structure amplitudes for scattering of sufficiently hard x rays[19] are primarily related to the Fourier transforms $\rho(\vec{g})$ of the crystal charge

TABLE I. Density-matrix coefficients for LiH crystals. Screening parameters for 1*s* functions are $\alpha_{\mathrm{Li}}=2.6875$ and $\alpha_{\mathrm{H}}=0.7724$. Two-center distances are in units of $a_0/2$.

Two-center distance	0	$\sqrt{2}$	$\sqrt{4}$	$\sqrt{6}$	$\sqrt{8}$	$\sqrt{10}$	$\sqrt{12}$
$T_{\mathrm{H\,H}}$	1.2447	-1.217×10^{-1}	1.782×10^{-2}	1.793×10^{-2}	7.088×10^{-3}	-2.929×10^{-3}	-5.647×10^{-3}
$T_{\mathrm{Li\,Li}}$	1.0175	4.822×10^{-3}	2.009×10^{-3}	-6.43×10^{-4}	-3.79×10^{-4}	-1.80×10^{-4}	1.26×10^{-4}
Two-center distance	1	$\sqrt{3}$	$\sqrt{5}$	$(\sqrt{9})_1$	$(\sqrt{9})_2$	$\sqrt{11}$	
$T_{\mathrm{Li\,H}}=T_{\mathrm{H\,Li}}$	-4.700×10^{-2}	1.123×10^{-2}	4.135×10^{-3}	-1.293×10^{-3}	-1.49×10^{-4}	-6.81×10^{-4}	

density. In LiH crystals we write

$$\rho_{\mathrm{LiH}}(\vec{g}) = \frac{1}{N_c}\int \rho(\vec{r},\vec{r})e^{i\vec{g}\cdot\vec{r}}d\vec{r} = \rho_{\mathrm{Li}}(\vec{g}) + \rho_{\mathrm{H}}(\vec{g}), \tag{15}$$

where we have divided $\rho_{\mathrm{LiH}}(\vec{g})$ into two contributions corresponding to the pseudoions

$$\rho_{\mathrm{Li}}(\vec{g}) = 2\sum_{\nu} T_{\mathrm{Li}\,\nu}\int \phi^{*}_{\mathrm{Li}}(\vec{r})\phi_{\nu}(\vec{r}-\vec{R}_{\nu}) \times e^{i\vec{g}\cdot\vec{r}}d\vec{r}\,; \tag{16a}$$

$$\rho_{\mathrm{H}}(\vec{g}) = 2e^{i\vec{g}\cdot\vec{d}_2}\sum_{\mu} T_{\mathrm{H}\mu}\int \phi^{*}_{\mathrm{H}}(\vec{r})\phi_{\mu}(\vec{r}-\vec{R}_{\mu}) \times e^{i\vec{g}\cdot\vec{r}}d\vec{r}\,; \tag{16b}$$

the sum over μ, ν runs over all neighbors of H and Li up to a given distance (to include in our calculations 179 ions). The phase factor $\exp(i\vec{g}\cdot\vec{d}_2)$ corresponding to the reciprocal-lattice vector $\vec{g} = (2\pi/a_0)(h,k,l)$ is $+1(-1)$ when h, k, l are all even (odd) integers.

We have here to consider certain *one- and two-center integrals involving both plane waves and* STO's. One-center integrals are immediate. The evaluation of two-center integrals is a technical but not trivial problem. Waller *et al.*[8] simplified calculations by performing a spherical average of the charge density with regard to each nucleus; this corresponds to expand the plane wave $e^{i\vec{g}\cdot\vec{r}}$ into spherical harmonics keeping only the zero-order Bessel function $j_0(gr)$. Kahane *et al.*[9] took into account higher-order spherical harmonics with a quite laborious procedure. In this paper we have found it very convenient to adopt the technique of Lafon and Lin[11] for the calculation of the matrix elements of $e^{i\vec{g}\cdot\vec{r}}$. This technique uses continuous Gaussian transforms of STO's and exploits the fact that a two-center product of Gaussians is a simple Gaussian on a third center; it is applicable[11] to $s, p, d, \ldots$, STO's, and allows straightforward calculations without performing spherical average of the charge density. The possibility of carrying out calculations without any spherical average is found to be important in LiH even if the pseudoions structure factors, Eqs. (16a) and (16b), are rather different; in the case, for instance, of diamond this possibility is even more important and allows the calculation of the structure amplitudes of "forbidden reflexions."

In Table II, we give the Fourier transforms $\rho_{\mathrm{LiH}}(\vec{g})$ including the neglecting overlap effects for comparison. The importance of overlap effects is evident.

In order to compare our calculations with experiment, we take into account the thermal effects in the usual way through the Debye-Waller factors. The structure factors are given by

$$F_{\mathrm{LiH}}(\vec{g}) = \rho_{\mathrm{Li}}(\vec{g})\exp\left(\frac{-B_{\mathrm{Li}}g^2}{16\pi^2}\right) + \rho_{\mathrm{H}}(\vec{g})\exp\left(\frac{-B_{\mathrm{H}}g^2}{16\pi^2}\right), \tag{17}$$

with $B_{\mathrm{Li}} = 1.1$ Å^2 and $B_{\mathrm{H}} = 1.8$ Å^2 as measured by Calder *et al.*[12] by x-ray and neutron diffraction. The results are reported in Table II together with the experimental results of Calder *et al.*; these measurements were put on absolute scale[12] by comparing reflexions from LiH with reflexions from NaCl. In order to check the agreement between theory and experiments we calculate the ratio

$$R = \frac{\sum \big|\,|F_{\mathrm{meas}}| - |F_{\mathrm{calc}}|\,\big|}{\sum |F_{\mathrm{meas}}|}, \tag{18}$$

and we obtain for the 21 independent reflexions measured by Calder *et al.*[12] the value $R_{21} = 0.0171$; for even and odd reflexions we have $R^{+}_{21} = 0.0130$ and $R^{-}_{21} = 0.0251$, respectively; these are indeed good values for this kind of experiments.

To compare our results with previous calculations[8,9] (and also to obtain a check independent from the precision of the absolute scale of Calder *et al.*[12]) we have normalized our calculated structure factors in such a way that $F_{200}(\mathrm{calc}) = F_{200}$ (meas), which is the strongest reflexion. Indicating by R_N the ratio, Eq. (18), after normalization, we obtain $R_{N\,21} = 0.0188$, $R^{+}_{N\,21} = 0.0151$, $R^{-}_{N\,21} = 0.0256$, which confirm the better agreement of our results with experiment with respect to previous calculations.[8,9]

For sake of completeness we have calculated structure factors in LiH with other values of the screening α_{H}, namely, $\alpha_{\mathrm{H}} = 0.7208$ (Lundqvist's calculation[2]), $\alpha_{\mathrm{H}} = 0.837$ (cluster approach[6]), and $\alpha_{\mathrm{H}} = 0.5715$ and $\alpha_{\mathrm{H}} = 1.0074$ for spin-up and spin-down electrons (Hurst's unrestricted Hartree-Fock calculation[14]). In Table III we report the ratio R of Eq. (18) and the ratio R_N after normalization for our calculations and those available in the literature. From Table III we see that the values of α_{H} of Hurst[14] and Lundqvist[2] give closer agreement with x-ray elastic scattering.

A rather subtle but interesting point is the comparison of the structure factor F_{333} with F_{511} (or similarly F_{442}, F_{600} and F_{551}, F_{711}). In a spherical averaged charge-density approximation we would have $F_{333} = F_{511}$ since the corresponding $|\vec{g}|$ are equal; thus the difference between F_{333} and F_{511} is sensitive to the deviations of charge density from spherical symmetry in the cubic fcc crystals. In the calculations of Kahane *et al.*[9] using Kunz[20] functions, the structure factors for

TABLE II. Fourier transforms of the charge density, and calculated and measured structure factors for LiH (electrons per molecular unit). Screening parameters for 1*s* functions are $\alpha_{\mathrm{Li}} = 2.6875$ and $\alpha_{\mathrm{H}} = 0.7724$.

Reciprocal-lattice vectors (units of $2\pi/a_0$)	Charge-density Fourier transforms without overlap	Charge-density Fourier transforms with overlap	Structure factors with overlap	Experimental structure factors of Calder *et al.* (Ref. 12)	Renormalized structure factors with overlap	Renormalized structure factors with overlap of Kahane *et al.* (Ref. 9)
(0, 0, 0)	4	4	4			
(1, 1, 1)	1.0709	1.0384	1.0096	1.086	0.9996	1.3670
(2, 0, 0)	2.0186	2.2140	2.0523	2.032	2.0320	2.0320
(2, 2, 0)	1.4452	1.6670	1.4480	1.454	1.4337	1.4720
(3, 1, 1)	0.9420	1.1361	0.9618	0.960	0.9523	0.9535
(2, 2, 2)	1.1157	1.3700	1.1121	1.096	1.1011	1.1560
(4, 0, 0)	0.8885	1.1620	0.8834	0.888	0.8747	0.9238
(3, 3, 1)	0.6575	0.9182	0.6796	0.671	0.6729	0.5835
(4, 2, 0)	0.7235	1.0091	0.7187	0.738	0.7116	0.7680
(4, 2, 2)	0.5934	0.8838	0.5888	0.600	0.5830	0.6434
(3, 3, 3)	0.4611	0.7390	0.4792	0.472	0.4745	0.3726
(5, 1, 1)	0.4611	0.7389	0.4791	0.474	0.4744	0.3926
(4, 4, 0)	0.4137	0.7007	0.4097	0.414	0.4056	0.4469
(5, 3, 1)	0.3284	0.6038	0.3430	0.354	0.3396	0.2648
(4, 4, 2)	0.3486	0.6299	0.3449	0.349	0.3415	0.3759
(6, 0, 0)	0.3486	0.6298	0.3448	0.359	0.3414	0.3531
(6, 2, 0)	0.2952	0.5692	0.2916	0.299	0.2887	0.2977
(5, 3, 3)	0.2372	0.4995	0.2485	0.248	0.2460	0.1893
(6, 2, 2)	0.2512	0.5171	0.2479	0.250	0.2454	0.2504
(4, 4, 4)	0.2152	0.4723	0.2120	0.209	0.2099	0.2175
(5, 5, 1)	0.1747	0.4209	0.1836	0.182	0.1818	0.1460
(7, 1, 1)	0.1747	0.4209	0.1836	0.179	0.1818	0.1581

TABLE III. Values of R and R_N for several choices of the screening parameter α_H; the value α_{Li} is 2.6875. All calculations include overlap effects; in the calculations reported in the last two columns the spherical average of charge density has been performed.

	$\alpha_H = 0.7208$	$\alpha_H = 0.7724$	$\alpha_H = 0.837$	$\alpha_H = 0.5715$ $\alpha_H = 1.0074$	Kahane *et al.* (Ref. 9)	Waller *et al.* (Ref. 8)	$\alpha_H = 0.7724$
R_{21}	0.0181	0.0171	0.0274	0.0225	···	···	0.0213
R^+_{21}	0.0158	0.0130	0.0216	0.0181	···	···	0.0178
R^-_{21}	0.0223	0.0251	0.0383	0.0307	···	···	0.0279
$R_{N_{21}}$	0.0150	0.0188	0.0402	0.0232	0.0769	···	0.0248
$R^+_{N_{21}}$	0.0091	0.0151	0.0247	0.0144	0.0303	···	0.0196
$R^-_{N_{21}}$	0.0262	0.0256	0.0694	0.0397	0.1645	···	0.0345
R_7						0.1833	
R_{N_7}						0.1057	

F_{333} and F_{511} (F_{442}, F_{600} and F_{551}, F_{711}) were not in the same trend as experiments. In our calculations of Table II we have a difference which is much smaller than that of experiments; also using the unrestricted Hartree-Fock screenings we do not obtain a substantial improvement under this aspect, despite the increase of the overlap between Li$^+$ and H$^-$ wave functions when $\alpha_H = 0.5715$. Were the experimental values at same $|\vec{g}|$ confirmed, it would be necessary for their explanation to improve the ionic picture for LiH allowing some mixing of 2s functions of lithium.

The main results and conclusions of this paper can be summarized as follows. (i) The density matrix in closed-shell crystals can be efficiently calculated setting up at a few selected $\vec{k}$ vectors the inverse of the overlap matrix between Bloch sums. In non-closed-shell crystals the sampling procedure of $\vec{k}$ vectors can be adopted, combined with a band-structure calculation. (ii) The computational technique of Lafon and Lin then allows simple calculations of x-ray structure factors, without spherical average of the charge density. It is thus possible to calculate differences in structure factors for independent reflexions with the same $|\vec{g}|$ and/or "forbidden reflexions," which are particularly sensitive to electronic wave functions responsible of crystal binding. (iii) In the case of LiH we have shown that screened hydrogenic wave functions, which explain Compton profile, are also in very good agreement with x-ray elastic scattering.

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