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Coherent Atomic Scattering Factors for the Lithium Hydride Crystal Field[*]

R. P. HURST[†]
University of Wisconsin Naval Research Laboratory, Madison, Wisconsin

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This paper describes an effort made to evaluate the coherent atomic scattering factors for the lithium and hydride ions as they exist in the LiH crystal field. The two electron wave functions chosen to describe these ions are each in turn optimized in the field of positive and negative point charges arranged as the corresponding ions are arranged in the crystal. Using the orbital exponents obtained from the minimization process, atomic scattering factor calculations are made in the usual way. The factors for Li^+ are unchanged. Interesting effects are noted for the H^- scattering factors.

The energy of the ions in the field of point charges is related to the crystal cohesive energy. Specifically, neglecting the zero-point energy correction, the calculated open configuration results were -236.3 and -227.4 kcal/mole when compared with computed and experimentally determined free H^- reference energies, respectively. The experimental cohesive energy is -218.5 kcal/mole.

Finally, it was noted that the H^- ion contracts in the crystal field. A possible explanation for this effect is given.

I. INTRODUCTION

THE atomic scattering factor or form factor may be thought of as a measure of the scattering due to the individual atoms. By nature and definition it is essentially an atomic property. Perhaps on the basis of this notion most of the recent effort expended in attempting to improve existing tables of these factors has been limited to using better atomic wave functions. To mention just a few examples, Thomas and Umeda[1] have recently published a very extensive table based on the Thomas-Fermi-Dirac model, Berghius[2] *et al.* have computed Hartree-Fock self-consistent field (SCF) factors for a large number of atoms and Hurst, Miller, and Matsen[3,4] have considered radial correlation for a number of two-, three-, and four-electron systems.

In view of the increasing interest of x-ray crystallographers in obtaining experimental information regarding the nature of chemical bonding, it seems necessary that the effects of the crystal field on the scattering factor be more fully treated. With this goal, the present effort is to evaluate the coherent atomic scattering factors for the lithium and hydride ions as they exist in the lithium hydride crystal field.

II. THE MODEL

The model chosen for this problem is a central two-electron ion surrounded by an infinite lattice of positive and negative point charges arranged as the corresponding ions are arranged in the crystal. First the wave function for the hydride ion is minimized with respect to the energy in the field of point charges and then the orbital exponents obtained by this minimization are used in the scattering factor calculation. Finally, this process is repeated for the case that the Li^+ species is the central ion. Essentially, in this model the crystal is assumed to be entirely ionic with no exchange between charge clouds of adjacent ions. These assumptions are supported at least partially by three lines of indirect experimental evidence which suggest an ionic type model:

(a) X-ray diffraction studies[5] of the lithium hydride crystal indicate that this crystal is of the well-known sodium chloride type, with lithium positive and hydrogen negative.

(b) The physical properties of crystalline lithium hydride are much like those of the halide salts of the alkali metals. For example, lithium hydride is a colorless, crystalline solid with a high melting point (680°C).

(c) Electrolysis of molten lithium hydride yields hydrogen at the anode.

III. METHODS AND CALCULATIONS

A. Formulation of the Problem

The wave function for the central ion is the so-called "open configuration" function of the form[6–8]

$$\Psi(1,2)=\begin{pmatrix}A & B\\ \alpha & \beta\end{pmatrix}+\begin{pmatrix}B & A\\ \alpha & \beta\end{pmatrix}, \tag{1a}$$

where A and B are $1s$ hydrogenic atomic orbitals centered on the central ion and having effective nuclear charges a and b, respectively. That is

$$A=\psi_{1s}(a)=(a^3/\pi)^{\frac{1}{2}}e^{-ar}, \tag{1b}$$

and

$$B=\psi_{1s}(b)=(b^3/\pi)^{\frac{1}{2}}e^{-br}. \tag{1c}$$

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[1] L. H. Thomas and K. Umeda, J. Chem. Phys. **26**, 293 (1957).

[2] Berghius, Hannappel, Potters, Loopstra, MacGillavry, and Weenendaal, Acta Cryst. **8**, 478 (1955).

[3] Hurst, Miller, and Matsen, Acta Cryst. **11**, 320 (1958).

[4] R. P. Hurst and F. A. Matsen, Acta Cryst. **12**, 7 (1959).

[5] For a summary of the properties of lithium hydride, see D. T. Hurd, *Chemistry of the Hydrides* (John Wiley & Sons, Inc., New York, 1952).

[6] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[7] C. Eckart, Phys. Rev. **36**, 878 (1930).

[8] $\begin{pmatrix}B & A\\ \alpha & \beta\end{pmatrix}=\frac{1}{(2!)^{\frac{1}{2}}}\begin{vmatrix}B(i)\alpha(i) & A(i)\beta(i)\\ B(j)\alpha(j) & A(j)\beta(j)\end{vmatrix}$.

This wave function was chosen as it allows for some radial correlation and enables one to obtain a reasonably good energy, at least in atomic calculations, without an unreasonable amount of labor. In particular, recent calculations [9–11] have shown that this type of function gives lower atomic energies than usually is obtained from the Hartree-Fock SCF method. The corresponding "closed configuration" wavefunction is obtained from Eqs. (1) by restricting the orbital exponents such that $a=b$.

The Hamiltonian can be written as the sum

$$H=H_0+H_1+H_2+H_3+\cdots. \tag{2}$$

Here H_0 is the Hamiltonian for the two electrons in the field of the central ion, H_1 represents the perturbation terms due to the group of first nearest neighbors, H_2 the perturbation due to the second nearest neighbors, etc. Thus, H_0 for electrons i and j of the central ions with nuclear charge Z is given in atomic units by

$$H_0=-\tfrac{1}{2}\nabla_i^2-\tfrac{1}{2}\nabla_j^2-\frac{Z}{r_i}-\frac{Z}{r_j}+\frac{1}{r_{ij}}. \tag{3}$$

The perturbation H_1 due to the group of six neighbors nearest the central ion is given by

$$\begin{aligned}H_1=p\biggl\{&\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\alpha+\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\beta\\&+\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\gamma+\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\delta\\&+\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\epsilon+\left(\frac{1}{r_1(i)}+\frac{1}{r_1(j)}\right)_\zeta-6\frac{Z}{R_1}\biggr\}.\end{aligned} \tag{4}$$

In explanation of the notation employed it is necessary to specify the electron, the particular group of neighbors involved, and the particular member of that group of neighbors. Thus, to keep the notation consistent the two electrons are specified by the letters i and j, the group of neighbors by an Arabic subscript, and the member of the group of neighbors by a Greek subscript. In addition, p is the total charge on the central ion, i.e., $p=1$ for Li^+ and $p=-1$ for H^-. Then, for example, $p[1/r_1(i)+1/r_1(j)]_\alpha$ gives the interaction of the electrons with the α member of the group of first nearest neighbors and $-6Zp/R_1$ gives the energy of attraction or repulsion between these first nearest neighbors and the nucleus of the central ion.

Since the approximate wave function [Eqs. (1)] is antisymmetric with respect to electron interchange, one can replace the terms $1/r_1(i)+1/r_1(j)$ of Eq. (4) by $2/r_1(i)$. Further, since the approximate wave function is spherically symmetric the perturbations due to the nearest neighbors are equivalent. Thus, we can omit the Greek subscripts and combine like terms to obtain,

$$H_1=6p\left(\frac{2}{r_1(i)}-\frac{Z}{R_1}\right). \tag{5}$$

Similarly for the next 12 nearest neighbors,

$$H_2=-12p\left\{\frac{2}{r_2(i)}-\frac{Z}{R_2}\right\}. \tag{6}$$

This can be generalized by comparing with the well-known Madelung series. For a sodium chloride type of crystal, such as is considered here, the Coulombic energy E_c due to a system of point charges is given in atomic units (a.u.) by

$$\begin{aligned}E_c=\frac{-A}{r}&=-\frac{1}{r}\left(\frac{6}{\sqrt{1}}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}+\cdots\right)\\&=-\frac{1}{r}\left(\frac{m_1}{\sqrt{1}}+\frac{m_2}{\sqrt{2}}+\frac{m_3}{\sqrt{3}}+\frac{m_4}{\sqrt{4}}+\cdots\right).\end{aligned} \tag{7}$$

Here r is the distance between nearest neighbors or half the length of the unit cell, A is the Madelung constant 1.747558, and R_n is the distance from the central ion to the nth layer of neighbors having $|m_n|$ ions. Then, by comparison with Eq. (7), we have

$$R_n=r\sqrt{m} \tag{8}$$

and

$$H_n=m_np\left(\frac{2}{r_n(i)}-\frac{Z}{R_n}\right);\quad n>0 \tag{9}$$

so that $m_1=6$, $m_2=-12$, $m_3=8$, $m_4=-6$, $\cdots$ etc.

One might suppose that the energy E could be computed in the usual way from

$$E=\int\Psi H\Psi d\tau\Big/\int\Psi\Psi d\tau. \tag{10}$$

This, however, is not practical due to the extremely poor convergence of the following sum comprising the numerator:

$$\int\Psi H\Psi d\tau=\int\Psi H_0\Psi d\tau+\int\Psi H_1\Psi d\tau+\int\Psi H_2\Psi d\tau+\cdots. \tag{11}$$

This is to be expected as it is well known that special techniques are required to evaluate the Madelung constant. This convergence difficulty can be overcome by making use of the asymptotic form of the interaction

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[9] Harrison Shull and Per-Olov Löwdin, J. Chem. Phys. **25**, 1035 (1956).

[10] Hurst, Gray, Brigman, and Matsen, Mol. Phys. **1**, 189 (1958).

[11] Brigman, Hurst, Gray, and Matsen, J. Chem. Phys. **29**, 251 (1958).

integrals. That is, since

$$\int \Psi H_n \Psi d\tau \Big/ \int \Psi\Psi d\tau$$

$$= \frac{2m_n p}{NR_n}\Bigg\{2-(1+aR_n)e^{-2aR_n}-(1+bR_n)e^{-2bR_n} + \frac{128(ab)^3}{(a+b)^6}\left[1-\left(1+\frac{(a+b)}{2}R_n\right)e^{-(a+b)R_n}\right]\Bigg\} - \frac{m_n p Z}{R_n}, \quad n>0 \qquad (12)$$

where N is the normalization integral

$$N=2+\frac{128(ab)^3}{(a+b)^6}, \qquad (13)$$

we have for large R_n

$$\int \Psi H_n \Psi d\tau \Big/ \int \Psi\Psi d\tau \rightarrow \frac{m_n p(2-Z)}{R_n}$$

$$\text{or} \quad \int \Psi H_n \Psi d\tau \Big/ \int \Psi\Psi d\tau \rightarrow -\frac{m_n}{R_n}, \qquad (14)$$

since when $p=1$, $Z=3$, and when $p=-1$, $Z=1$. That is, at sufficiently large R_n the interaction energy as computed from Eq. (12) is equal to that which would be obtained if the central ion were a point charge.

Essentially then, in using this fact to obtain convergence of Eq. (11), the energy is initially computed from the assumption that all neighbors view the central ion as a point charge. Later, for those neighbors sufficiently close to the central ion that the interaction energy cannot be computed in this way the incorrect interaction energy is subtracted out and the correct value for the interaction energy as given by Eq. (12) is added in.

This process is performed as follows. First E_{00}, the energy of the central ion by itself, is computed. E_{00} is given by

$$E_{00}=\int \Psi H_0 \Psi d\tau \Big/ \int \Psi\Psi d\tau = \int \Psi H_0 \Psi d\tau \Big/ N, \qquad (15)$$

where

$$\int \Psi H_0 \Psi d\tau = 2\Bigg[a(\tfrac{1}{2}a-Z)+b(\tfrac{1}{2}b-Z) + \frac{64(ab)^3}{(a+b)^5}\left(\frac{ab}{a+b}-Z\right)+\frac{ab(a^2+3ab+b^2)}{(a+b)^3} + 20\frac{(ab)^3}{(a+b)^5}\Bigg]. \qquad (16)$$

Next, the energy E_0, representing the energy of the central ion plus the Coulombic interaction energy that would result if the central ion were a point charge is computed from

$$E_0=E_{00}+E_c=\left(E_{00}N-\frac{A}{R_1}N\right)\frac{1}{N}, \qquad (17)$$

where A is the Madelung constant and E_c is the Coulombic energy as given in Eq. (7).

Next, E_0 is improved by correcting the interaction energy due to the group of first nearest neighbors. Thus, E_1 is obtained from E_0 by subtracting out the incorrect value $-m_1/R_1$, which was taken as the interaction energy of these six nearest neighbors with the central ion, and putting in its place $\int \Psi H_1 \Psi d\tau / \int \Psi\Psi d\tau$. Here again H_1 is given by Eq. (5). Then E_1 is obtained from

$$E_1=\left[E_0N-6\left\{\frac{(pZ-1)N}{R_1}+2pB_1\right\}\right]\frac{1}{N}, \qquad (18)$$

where

$$B_1=-\int \frac{\Psi\Psi}{r_1(i)}d\tau. \qquad (19)$$

Similarly, by correcting the second nearest neighbor interaction energy one obtains E_2 from E_1 using

$$E_2=\left[E_1N+12\left\{\frac{(pZ-1)}{R_2}N+2pB_2\right\}\right]\frac{1}{N}, \qquad (20)$$

and E_3 from

$$E_3=\left[E_2N-8\left\{\frac{(pZ-1)}{R_3}N+2pB_3\right\}\right]\frac{1}{N}. \qquad (21)$$

By induction one may show that in general

$$E_{n+1}=\left[E_nN-m_n\left\{\frac{(pZ-1)}{R_n}N+2pB_n\right\}\right]\frac{1}{N}, \quad n\geq 0. \qquad (22)$$

Again, the numbers m_n are taken from the terms in the Madelung series [see Eq. (7), $R_n=(n)^{\frac{1}{2}}r$, p is the total charge on the central ion, N is the normalization constant given by Eq. (13), and B_n is given by

$$B_n=-\int \frac{\Psi\Psi}{r_n(i)}d\tau$$

$$=-\frac{1}{R_n}\Bigg\{2-(1+aR_n)e^{-2aR_n}-(1+bR_n)e^{-2bR_n} - \frac{128(ab)^3}{(a+b)^6}\left[1-\left(1+\frac{(a+b)}{2}R_n\right)e^{-(a+b)R_n}\right]\Bigg\}. \qquad (23)$$

The iterations indicated by Eq. (22) were applied until E_{n-2}, E_{n-1}, and E_n agreed with each other to at least six significant figures. This limiting value of E_n will hereafter be referred to as E.

Two cases were considered, H^- as the central ion and Li^+ as the central ion. For both cases E was minimized with respect to the orbital exponents a and b by a scheme previously developed for minimizing atomic wave functions.[10] Essentially, in this method a set of orbital exponents $X_1^1, X_1^2, X_1^3, \cdots, X_1^n$ are chosen and a calculation of the energy E is made. (In this case there are only two exponents a and b.) Next, energy calculations are made using the orbital exponents X_0^1, $X_1^2, \cdots X_1^n$ and $X_2^1, X_1^2, \cdots, X_1^n$, where $X_0^1-X_1^1=-\Delta$ and $X_2^1-X_1^1=\Delta$ and where Δ is an arbitrary difference roughly the same order of magnitude as the expected error in that orbital exponent. Then these results are used to obtain an improved orbital exponent X_*^i from the equation

$$X_*^i=\frac{X_0^i+X_1^i}{2}-\frac{\Delta[E(X_1^i)-E(X_0^i)]}{E(X_0^i)-2E(X_1^i)+E(X_2^i)},\quad i=1,2,\cdots n. \tag{24}$$

Using this improved result for X_1^1, the next exponent X_1^2 is improved and so forth until all the exponents have been improved. Finally, one begins again with the first exponent, gradually reducing Δ until no changes in the exponents are obtained.

Using the optimized orbital exponents a and b obtained by the process just described, the atomic scattering factors were computed in the usual way from[3,12]

$$f=\int\Psi^*\sum_k e^{i\mu\cos\alpha_k r_k}\Psi d\tau\bigg/\int\Psi^*\Psi d\tau, \tag{25}$$

$$f=\frac{1}{N}\left\{\frac{32a^4}{(4a^2+\mu^2)^2}+\frac{256(ab)^3}{[(a+b)^2+\mu^2]^2(a+b)^2}+\frac{32b^4}{(4b^2+\mu^2)^2}\right\}, \tag{26}$$

where N is given by Eq. (13) and

$$\mu=4\pi\sin\theta/\lambda\ (\text{a.u.})^{-1}. \tag{27}$$

B. Relation Between E and the Crystal Energy E_{cry}

An important check on the correctness of this model is the comparison of the computed lattice energy E_{cry} with the experimentally determined Born-Haber cycle energy. We will now consider how the energy E as computed in Sec. III-a is related to E_{cry}.

First of all we shall assign to each hydride ion a number in the range $1, 2, \cdots, N$ and to each lithium ion a number in the range $N+1, N+2, \cdots, 2N$. Further, we shall denote the interaction between the ith and jth ions by ϕ_{ij}. Since a given ion cannot react with itself, it is convenient to define $\phi_{ii}=0$.

Then, adopting these conventions, the total interaction due to the $2N$ ions in the crystal is given by ϕ, where

$$\phi=\sum_{i=1}^{2N}\sum_{j=i+1}^{2N}\phi_{ij}, \tag{28}$$

or

$$\phi=\sum_{i=1}^{2N}\sum_{j=1}^{j=i}\phi_{ij}. \tag{29}$$

Thus, on adding Eqs. (28) and (29), we have

$$\phi=\tfrac{1}{2}\sum_{i=1}^{2N}\sum_{j=1}^{2N}\phi_{ij}. \tag{30}$$

Next, to isolate the types of interaction involved, Eq. (30) is regrouped to give

$$\phi=\tfrac{1}{2}\sum_{i=1}^{2N}\Big[\sum_{j=1}^{N}\phi_{ij}+\sum_{j=N+1}^{2N}\phi_{ij}\Big], \tag{31}$$

or

$$\begin{aligned}\phi&=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\phi_{ij}+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=N+1}^{2N}\phi_{ij}+\tfrac{1}{2}\sum_{i=N+1}^{2N}\sum_{j=1}^{N}\phi_{ij}+\tfrac{1}{2}\sum_{i=N+1}^{2N}\sum_{j=N+1}^{2N}\phi_{ij}\\&=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\phi_{ij}+\sum_{i=1}^{N}\sum_{j=N+1}^{2N}\phi_{ij}+\tfrac{1}{2}\sum_{i=N+1}^{2N}\sum_{j=N+1}^{2N}\phi_{ij}.\end{aligned} \tag{32}$$

Neglecting surface effects, each lithium is equivalent to each other lithium ion and each hydride ion is equivalent to every other hydride ion so that Eq. (32) can be written

$$\phi=N\Big[\tfrac{1}{2}\sum_{j=1}^{N}\phi_{kj}+\sum_{j=N+1}^{2N}\phi_{kj}+\tfrac{1}{2}\sum_{j=N+1}^{2N}\phi_{rj}\Big], \tag{33}$$

where

$$k\leq N,\quad r>N.$$

To clarify the meaning of this result, Eq. (33) can be written,

$$\phi=\tfrac{1}{2}\sum_{j=1}^{N}(H_k-H_j)+\sum_{j=N+1}^{2N}(H_k-L_j)+\tfrac{1}{2}\sum_{j=N+1}^{2N}(L_r-L_j). \tag{34}$$

The first and second terms on the right side of Eq. (34) represent the interaction of the kth hydride ion with the other hydride and lithium ions, respectively. Similarly, the last term gives the interaction of the rth lithium ion with the other lithium ions. The interactions are to be expressed in atomic units per mole thus eliminating the necessity of multiplying by N.

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[12] The middle term on the right-hand side of Eq. (26) has previously been incorrectly reported as $256(ab)^4/\{[(a+b)^2+\mu^2]^2(a+b)^2\}$. See reference 3.

TABLE I. Crystal energy results (in atomic units, except where otherwise specified).

	Open configuration $a=1.0074$; $b=0.57146$	Closed configuration $a=b=0.77242$
E_{00}	-0.481560	-0.465445
E_0	-0.934296	-0.918180
E_1	-0.886192	-0.886345
E_2	-0.898068	-0.891334
E_3	-0.896340	-0.890852
E_4	-0.896711	-0.890924
E_5	-0.896208	-0.890855
E_6	-0.896399	-0.890874
E_8	-0.896416	-0.890875
E_9	-0.896396	-0.890874
E_{10}	-0.896404	-0.890874
E_{11}	-0.896400	-0.890874
E_{12}	-0.896401	-0.890874
E_{13}	-0.896400	-0.890874
E_{14}	-0.896401	-0.890874
E_{16}	-0.896401	-0.890874
$E_{17}=E$	-0.896401	-0.890874
E_{cry}[a] (calc. H^-)	-236.3 kcal/mole	-260.6 kcal/mole
E_{cry}[a] (exp. H^-)	-227.4 kcal/mole	-226.2 kcal/mole
Born-Haber E_{cry}[b]	-218.5 kcal/mole	

[a] The computed and experimental energies of the free H^- ions were taken from Shull and Löwdin [J. Chem. Phys. **25**, 1036 (1956)].

[b] Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 390.

Finally, E_{cry} is given by

$$E_{cry}=\Delta E_H+\Delta E_L+\phi,$$

or

$$E_{cry}=\Delta E_H+\Delta E_L+\tfrac{1}{2}\sum_{j=1}^{N} H_k-H_j + \sum_{j=N+1}^{2N} H_k\text{-}L_j+\tfrac{1}{2}\sum_{j=N+1}^{2N} L_r-L_j, \qquad (35)$$

where ΔE_H and ΔE_L are the differences between the energies of these ions in the crystal field and the free ion energies. The manner Eq. (35) is actually applied to compute E_{cry} is best understood in terms of the numerical results, hence this explanation will be deferred to the next section.

IV. RESULTS

The energies E were obtained as is indicated by Eqs. (15)–(23) and the optimum orbital exponents a and b were evaluated using Eq. (25). The calculations were made for the experimental lattice parameter $r=a_0/2=3.86$ a.u. All computations were made on an IBM CPC computer.

In the case of the hydride ion the optimum orbital exponents in the crystal field are $a=1.00746$ and $b=0.57146$ for the open-configuration calculation and $a=b=0.77242$ for closed-configuration calculation. These values may be compared with the free hydride ion exponents $a=1.0392$, $b=0.28319$, and $a=b=0.6875$ for the open- and closed-configuration calculations, respectively.

For the lithium ion the optimum orbital exponents in the crystal field are the same as those for the free ion, i.e., $a=3.2949$ and $b=2.0789$ for the open-configuration calculation and $a=b=2.6875$ for the closed-configuration calculation. For this ion the mean electron distribution is sufficiently near the nucleus that E is given by E_0 [Eq. (17)]. This means that to the accuracy of the calculation the lithium ion is a point charge and is not polarized by the crystal field.

In view of these results it would seem most consistent with the model to take $\Delta E_L=0$ in Eq. (35) when computing the lattice energy E_{cry}. Further, since the lithium ion is much smaller than the hydride ion, as is evidenced by the relative sizes of the orbital exponents, the Li^+-H^- interactions are best computed when the lithium is taken as the point charge rather than when the lithium is represented as a two-electron distribution and the hydride ion is taken as the point charge. Thus, in computing E_{cry} we shall not average the interaction energies obtained for H^- and Li^+ in the field as might seem suggested by Eq. (35).

The differences $E_{n+1}-E_n$ [see Eq. (22)] represent the correction due to the fact that the $n+1$ group of ions does not view the central ion as a point charge. Since this difference is always about zero for the case that Li^+ is the central ion, by applying Eq. (35) we can express E_{cry} in the following form:

$$E_{cry}=E_1-E_{H^-}+\tfrac{1}{2}(E_2-E_1)+(E_3-E_2)+\tfrac{1}{2}(E_4-E_3) +(E_5-E_4)+\tfrac{1}{2}(E_6-E_5)+\tfrac{1}{2}(E_8-E_6) +(E_9-E_8)+\cdots. \qquad (36)$$

TABLE II. Atomic scattering factors for the hydride ion.

Sinθ/λ ($A^{\circ -1}$)	Open configuration		Closed configuration		Hydrogen atom
	Crystal field	Free ion	Crystal field	Free ion	Field-free
0.000	2.0000	2.0000	2.0000	2.0000	1.0000
0.025	1.9503	1.8591	1.9545	1.9428	0.9863
0.050	1.8136	1.5659	1.8268	1.7851	0.9469
0.075	1.6200	1.2865	1.6403	1.5620	0.8863
0.100	1.4028	1.0638	1.4236	1.3137	0.8108
0.125	1.1881	0.8867	1.2028	1.0727	0.7271
0.150	0.9913	0.7417	0.9962	0.8586	0.6413
0.175	0.8194	0.6207	0.8140	0.6790	0.5581
0.200	0.6739	0.5193	0.6597	0.5339	0.4808
0.225	0.5530	0.4344	0.5325	0.4193	0.4111
0.250	0.4538	0.3635	0.4294	0.3300	0.3497
0.275	0.3731	0.3044	0.3469	0.2609	0.2966
0.300	0.3075	0.2554	0.2811	0.2074	0.2513
0.325	0.2544	0.2148	0.2287	0.1661	0.2128
0.350	0.2113	0.1811	0.1871	0.1339	0.1804
0.375	0.1763	0.1531	0.1538	0.1087	0.1532
0.400	0.1478	0.1299	0.1272	0.08894	0.1304
0.425	0.1244	0.1106	0.1059	0.07327	0.1113
0.450	0.1053	0.09455	0.08857	0.06078	0.09534
0.475	0.08951	0.08110	0.07452	0.05076	0.08190
0.500	0.07644	0.06982	0.06305	0.04266	0.07059
0.550	0.05650	0.05233	0.04585	0.03067	0.05299
0.600	0.04247	0.03979	0.03399	0.02254	0.04033
0.650	0.03243	0.03067	0.02566	0.01689	0.03110
0.700	0.02512	0.02394	0.01969	0.01288	0.02429
0.750	0.01972	0.01892	0.01533	0.009980	0.01919
0.800	0.01567	0.01512	0.01210	0.007843	0.01534
0.850	0.01259	0.01221	0.009662	0.006243	0.01238
0.900	0.01022	0.009949	0.007805	0.005028	0.01009
0.950	0.008377	0.008183	0.006368	0.004092	0.008299
1.000	0.006925	0.006785	0.005244	0.003362	0.006881
1.100	0.004846	0.004772	0.003646	0.002330	0.004838
1.200	0.003486	0.003446	0.002610	0.001663	0.003493
1.300	0.002568	0.002547	0.001915	0.001218	0.002581

Here the E_n are computed from Eq. (22) with H^- chosen as the central ion, E_{H^-} is the energy of the free hydride ion, and the polarization energy of Li^+, ΔE_L, is taken to be zero.

In Table I are summarized the crystal energy results for the open and closed configuration calculations. In Table II are given the scattering factors for H^- as computed from Eqs. (26) and (27). The factors for Li^+ have previously been published,[3] and hence will not be given here. Finally, the factors for the hydride ion are compared graphically in Fig. 1.

V. DISCUSSION

Nonempirical calculations of the lattice energy of LiH have previously been made by Hylleraas[13] and Lundquist.[14] Hylleraas obtained the result −219 kcal/mole and Lundquist's work gave −205 kcal/mole. In addition, Ewing and Seitz[15] have considered the general symmetry problems of constructing a proper wave function for this crystal.

In the present work the emphasis has not been on obtaining a good description of the lattice energy *per se*, rather it has been on attempting to approximate the charge clouds of the ions as they exist in the crystal so that the scattering factor calculations could be made. Nevertheless the open-configuration lattice energies are still in fair agreement with the Born-Haber cycle energy.

In this work no correction has been made for the zero-point energy as the various treatments for this quantity have given widely differing results.[16] Even with this correction the computed lattice energies still would be too large. This is as should be expected from the nature of the model used. It is reasonable to suppose, if the neighbor ions were replaced by distribution functions, that the lattice energies would be somewhat improved without radically changing the effective nuclear charge on hydrogen.

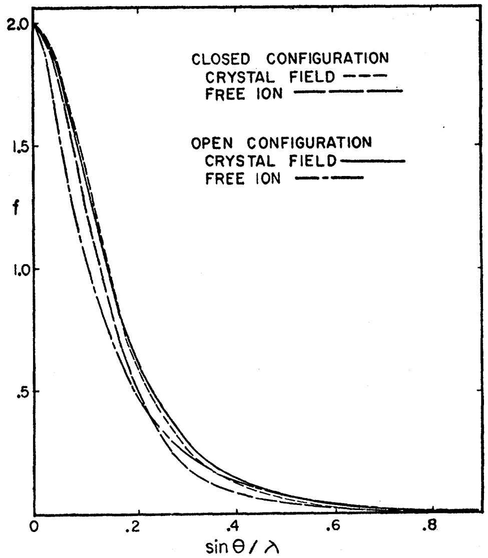

FIG. 1. Comparison of atomic scattering factors for H^-.

Finally, it is of interest to note that the hydride ion contracts in the crystal field as is evidenced by the larger orbital exponents for this ion in the field as compared with those for the ion out of the field. Since the hydride ion is surrounded by six nearest neighbor positive charges, superficial examination might suggest that the charge cloud would be spread out. It is well to note in this connection, however, that the magnitude of the interaction between these first nearest neighbor point charges and the electrons of H^- would be at a maximum if the central ion were a point charge. For this reason, the central hydride ion contracts until the interaction is offset by the increases in kinetic energy and electron-electron repulsion energies. This is analogous to Weinbaum's[17] findings for the hydrogen molecule. In his treatment using a wave function consisting of a Heitler-London type covalent term plus an ionic structure, the optimum effective nuclear charge is 1.193 for both structures together while the optimum effective nuclear charges are 1.0000 and 0.6875 for the free hydrogen atom and ion, respectively. Here the presence of the other positive nucleus contracts the charge cloud. Weinbaum's finding have been largely confirmed by the later work of Altmann and Cohen.[18]

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