negligible at low pressures. The values of the potential constants which give a fit to the data, $\sigma = 2.75$ Å, $\epsilon = 51.7 \times 10^{-16}$ ergs, differ at most by only a few percent from those given by gas phase data, $\sigma = 2.75$ Å, $\epsilon = 49.2 \times 10^{-16}$ ergs.

The fact that different constants are needed to explain the gas and solid-phase data of neon should not be at all surprising. The Mie–Lennard-Jones potential is a phenomenological interaction and should be expected to vary somewhat from one type of phenomenon to another.[14] A similar situation occurs, for example, in the treatment of argon. Second virial coefficient data[15] give, $\epsilon = 165 \times 10^{-16}$ ergs, gas viscosity data[16] give

$\epsilon = 171 \times 10^{-16}$ ergs, and crystal data[17] give $\epsilon = 169 \times 10^{-16}$ ergs.[18]

## ACKNOWLEDGMENTS

[14] See, for example, Ref. 10, p. 208.
[15] E. Whalley and W. G. Schneider, J. Chem. Phys. 23, 1644 (1955).
[16] H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 938 (1942).

[17] C. Domb and I. J. Zucker, Nature 178, 484 (1956).
[18] A small change of potential parameters may not account for the experimental data of the heavier inert gas solids. See the P-V data and discussion of C. A. Swenson for xenon [International Conference on the Physics and Chemistry of High Pressures (Society of the Chemical Industry, London, June, 1962)]. It may be necessary to include the effects of many-body forces to correlate the properties of solid xenon.

# Positronium in a LiH Crystal*

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The question as to whether the existence of a bound positronium-like system in an ionic crystal is energetically possible is considered with particular reference to lithium hydride. The crystal field of LiH is simulated by a potential expressed as a sum of central field potentials centered on the ion sites. An upper bound is obtained for the ground-state energy of a system of an electron and a positron in Coulomb interaction with each other and moving in the crystal potential, and comparison is made with estimates of the energies of the positron and the electron moving independently in the crystal. The result is energetically favorable to the formation and persistence of positronium in the crystal through capture by a positron of an electron from the valence band.

## I. INTRODUCTION

CONSIDERATION of possible mechanisms for the annihilation of positrons in ionic crystals gives rise to the question as to whether positronium, or more precisely a positronium-like bound system, can be formed and persist for an appreciable time in such a crystal. This question has formerly, on the basis of qualitative arguments, been answered in the negative.[1,2] It would appear desirable to reconsider the matter on a more quantitative basis.

In the following, we consider in Sec. II the simulation of the crystal field of LiH by means of a suitable potential. In Sec. III we consider the problem of a system of a positron and an electron in Coulomb interaction moving in the constant periodic potential of the crystal, the potential energy of the positron as a function of position being taken to be simply the negative of that of

the electron. By treating the effect of the crystal field as a perturbation of the Hamiltonian for free positronium, the energy shift of the ground state is calculated to second order of perturbation theory. An improved result is then obtained in the form of an upper bound to the ground-state energy by calculating the average of the Hamiltonian with the aid of a wave function given by perturbation theory. In Sec. IV the procedure used in estimating the ground-state energy of a positron in the crystal field is outlined. In Sec. V use is made of the results obtained in a discussion of the energetics of positronium formation in the crystal. Section VI contains an assessment of the results and their relation to experiment.

## II. CRYSTAL POTENTIAL OF LiH

The lithium hydride crystal, being an ionic crystal, has a relatively open structure. We therefore make the approximation of treating the potential as being made up of a sum of spherically symmetric potentials centered on the ion sites. The first problem, then, is to obtain an

[1] R. A. Ferrell, Rev. Mod. Phys. 28, 308 (1956).
[2] P. R. Wallace, Solid State Physics (Academic Press Inc., New York, 1960), Vol. 10.

approximation to the potential due to a lithium ion and that due to a hydride ion.

We shall take the potential due to a lithium ion to be of the form

$$\mathcal{V}_1(R) = (e/R) + (2e/R)e^{-\alpha R}, \quad (1)$$

where $e$ is the charge on a proton and $\alpha$ is a parameter which is to be determined. This potential has the correct behavior for both large and small $R$. It has the advantage of being simple in its mathematical form. Similarly, the potential of the hydride ion is taken to be

$$\mathcal{V}_2(R) = (2e/R)e^{-\beta R} - (e/R), \quad (2)$$

where $\beta$ is a parameter which is to be determined.

The parameter $\alpha$ is obtained by observing that the potential $\mathcal{V}_1(R)$ is effectively the potential in which the third electron of a lithium atom moves. The ground-state energy of this third electron is known. We may, therefore, set up the Schroedinger equation for this particle, wherein only the parameter $\alpha$ is unknown. With a fixed value of $\alpha$ we may solve the equation numerically. The parameter $\alpha$ can be varied until we obtain a solution which has one radial node and which behaves properly as $r \to \infty$. This procedure was carried out on a computer, and the value for $\alpha$ obtained was

$$\alpha = 4.152 \text{ Å}^{-1}. \quad (3)$$

The value for the parameter $\beta$ in the hydride ion potential was obtained in a different fashion. Using a wave function for the hydride ion, the charge density is

$$\rho(\mathbf{R}_1) = -2e \int_\tau |\psi(\mathbf{R}_1, \mathbf{R}_2)|^2 d\tau_2. \quad (4)$$

The potential due to this charge density, $v(R)$, is given by

$$\nabla^2 v(\mathbf{R}) = -4\pi\rho(\mathbf{R}). \quad (5)$$

The wave function for the hydride ion was taken to be of the form used by G. Darewych.[3]

$$\psi(\mathbf{R}_1, \mathbf{R}_2) = (1 + \nu R_{12})(e^{-(\lambda R_1 + \mu R_2)} + e^{-(\mu R_1 + \lambda R_2)}), \quad (6)$$

where

$$R_{12} = |\mathbf{R}_2 - \mathbf{R}_1|, \quad (7)$$

and

$$\lambda = 0.9033 \text{ Å}^{-1},$$
$$\mu = 2.0315 \text{ Å}^{-1}, \quad (8)$$
$$\nu = 0.5898 \text{ Å}^{-1}.$$

Using this wave function, it is possible to carry out the integration in Eq. (4) and to solve the Poisson equation to give an explicit form of the potential. This potential was approximated with high accuracy by the form

$$\mathcal{V}_2(R) = (2e/R)e^{-\beta R} - (e/R). \quad (9)$$

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[3] G. Darewych (private communication).

The value of $\beta$ for the best fit is

$$\beta = 1.715 \text{ Å}^{-1}. \quad (10)$$

The crystal potential is now taken to be

$$V(\mathbf{R}) = \sum_j [\mathcal{V}_1(\mathbf{R} - \mathbf{R}_j) + \mathcal{V}_2(\mathbf{R} - \mathbf{R}_j - \mathbf{a})], \quad (11)$$

where $\mathbf{R}_j$ is the position vector of the $j$th positive ion and $\mathbf{a}$ is the position vector of a negative ion with respect to an origin at the location of a positive ion.

## III. GROUND-STATE ENERGY OF POSITRONIUM IN THE CRYSTAL

We shall now investigate the problem of positronium in this potential. The Hamiltonian for the two-particle system in this field is

$$H = -(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) - (e^2/|\mathbf{r}_2 - \mathbf{r}_1|) + eV(\mathbf{r}_1) - eV(\mathbf{r}_2), \quad (12)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the positron and electron, respectively. It is to be noted that the potential energies of the electron and of the positron due to the crystal field differ only in sign.

The Hamiltonian may be expressed in terms of the center-of-mass coordinate $\mathbf{R}$ and the relative coordinate $\mathbf{r}$, where we have

$$\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \quad (13)$$

and

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1. \quad (14)$$

The Hamiltonian becomes

$$H = -\frac{\hbar^2}{4m}\nabla_R^2 - \frac{\hbar^2}{m}\nabla_r^2 - \frac{e^2}{r} + eV\left(\mathbf{R} - \frac{\mathbf{r}}{2}\right) - eV\left(\mathbf{R} + \frac{\mathbf{r}}{2}\right). \quad (15)$$

In accordance with perturbation theory, we write this Hamiltonian as the sum of two parts:

$$H = H_0 + H_1, \quad (16)$$

where

$$H_0 = -\frac{\hbar^2}{4m}\nabla_R^2 - \frac{\hbar^2}{m}\nabla_r^2 - \frac{e^2}{r} \quad (17)$$

and

$$H_1 = eV\left(\mathbf{R} - \frac{\mathbf{r}}{2}\right) - eV\left(\mathbf{R} + \frac{\mathbf{r}}{2}\right). \quad (18)$$

$H_1$ will be treated as a perturbation on the Hamiltonian $H_0$.

$H_0$ consists of the sum of two noninteracting parts,

$$-(\hbar^2/4m)\nabla_R^2 \quad (19)$$

and

$$-(\hbar^2/m)\nabla_r^2 - (e^2/r). \quad (20)$$

The first is the Hamiltonian of a free particle and the second is the Hamiltonian of the positronium atom. Therefore, the eigenfunctions of $H_0$ may be written

$$\psi_{k,nlm} = e^{ik\cdot R}\phi_{nlm}(\mathbf{r}), \tag{21}$$

where $\phi_{nlm}(\mathbf{r})$ is a positronium wave function, where the quantum numbers $n$, $l$, $m$ have the usual meaning. The energy corresponding to this state is

$$(\hbar^2 k^2/4m) + E_n, \tag{22}$$

where $E_n$ is the energy of the $n$th level of positronium.

Let us examine the effect of the perturbation on the ground-state energy. The first-order perturbation energy is

$$[\psi_{0,100}(\mathbf{r}), H_1\psi_{0,100}(\mathbf{r})]. \tag{23}$$

Since $H_1$ is of odd parity in the $\mathbf{r}$ space, this vanishes. From similar parity arguments, it can be seen that all odd-order perturbation energies vanish. Thus the second-order perturbation, which we shall now calculate, is in fact accurate to third order.

The second-order perturbation energy is

$$\sum_{k,nlm} \frac{|[\psi_{0,100}(\mathbf{r}), H_1\psi_{k,nlm}(\mathbf{r})]|^2}{E_1 - [(\hbar^2 k^2/4m) + E_n]}. \tag{24}$$

The inner product in the above expression involves an integration over both the $\mathbf{R}$ and the $\mathbf{r}$ spaces. The functions of $\mathbf{R}$ are not quadratically integrable, so we must resort to a box quantization procedure. The inner product becomes

$$\text{Lim}_{L\to\infty} \frac{1}{L^3} \int_{\tau_R, \tau_r} \phi_{100}{}^*(r)\left[ eV\left(\mathbf{R} - \frac{\mathbf{r}}{2}\right) - eV\left(\mathbf{R} + \frac{r}{2}\right)\right]$$
$$\times \phi_{nlm}(\mathbf{r}) e^{ik\cdot R} d\tau_R d\tau_r, \tag{25}$$

where $1/L^3$ is the square of the normalization constant used in the box quantization procedure. By suitable shifts of origin, expression (25) can be reduced to the form

$$\left[ \text{Lim}_{L\to\infty} \frac{1}{L^3} \int_{\tau_R} e^{ik\cdot R} eV(\mathbf{R}) d\tau_R \right]$$
$$\times \left[ \int_{\tau_r} \phi_{100}{}^*(r)\phi_{nlm}(\mathbf{r}) (e^{ik\cdot(r/2)} - e^{-ik\cdot(r/2)}) d\tau_r \right]. \tag{26}$$

Now $V(\mathbf{R})$ has the periodicity of the crystal. It may therefore be expanded as a Fourier series.

$$V(\mathbf{R}) = \sum C_K e^{2\pi iK\cdot R}, \tag{27}$$

where $\mathbf{K}$ is a vector of the reciprocal lattice.

The integral

$$\text{Lim}_{L\to\infty} \frac{1}{L^3} \int_{\tau_R} e^{ik\cdot R} V(\mathbf{R}) d\tau_R \tag{28}$$

is equal to $C_{-K}$, if $\mathbf{k}$ is $2\pi$ times a reciprocal lattice vector and is zero otherwise. Also, it is obvious that $C_K = C_{-K}$. Substituting these results into Eq. (26), we find that the second-order perturbation, expression (24), reduces to

$$4\sum_K |C_K|^2 \sum_{nlm} \frac{\left| \int \phi_{100}{}^*(\mathbf{r})\phi_{nlm}(\mathbf{r}) \sin\left(\frac{k\cdot r}{2}\right) d\tau_r \right|^2}{E_1 - \left(\frac{\hbar^2 k^2}{4-m} + E_n\right)}. \tag{29}$$

Now $E_n = E_1/n^2$. As $n$ increases $E_n$ quickly becomes small. We set $E_n$ equal to zero, in the above, in order to facilitate summations. We shall come back later and correct for the first few terms. Using this approximation, (29) may now be written

$$4\sum_K |C_K|^2 \sum_{nlm} \frac{\int \phi_{100}{}^*(r)\phi_{100}(r')\phi_{nlm}(\mathbf{r})\phi_{nlm}{}^*(\mathbf{r}') \sin\left(\frac{k\cdot r}{2}\right) \sin\left(\frac{k\cdot r'}{2}\right) d\tau_r d\tau_{r'}}{E_1 - \frac{\hbar^2 k^2}{4m}}. \tag{30}$$

We now sum over $n$, $l$, and $m$. Since $\{\phi_{nlm}(\mathbf{r})\}$ is a complete orthonormal set of functions, we have

$$\sum_{nlm} \phi_{nlm}{}^*(\mathbf{r}')\phi_{nlm}(\mathbf{r}) = \delta(\mathbf{r}' - \mathbf{r}). \tag{31}$$

Integration over the $\mathbf{r}'$ space reduces the integral to

$$4\sum_K |C_K|^2 \frac{\int |\phi_{100}(r)|^2 \sin^2\left(\frac{k\cdot r}{2}\right) d\tau_r}{E_1 - \frac{\hbar^2 k^2}{4m}}, \tag{32}$$

which is equal to

$$2\sum_K |C_K|^2 \frac{\{1 - [1/(1 + a_0^2 k^2)^2]\}}{E_1 - (\hbar^2 k^2/4 - m)}. \tag{33}$$

We must now evaluate $C_K$. From Eq. (27) we obtain

$$C_K = \frac{1}{\Delta} \int V(\mathbf{R}) e^{-2\pi iK\cdot R} d\tau_R, \tag{34}$$

where $\Delta$ is the volume of a unit cell of the crystal lattice and the integration is carried out over this volume.

Substituting Eq. (11) in (34) we obtain

$$C_K = \frac{1}{\Delta} \int \sum_j [\mathcal{U}_1(R-R_j) + \mathcal{U}_2(R-R_j-a)]$$
$$\times e^{-2\pi i K \cdot R} d\tau_R . \quad (35)$$

It is easily seen that this is equal to

$$\frac{1}{\Delta} \int [\mathcal{U}_1(R) + \mathcal{U}_2(R-a)] e^{-2\pi i K \cdot R} d\tau_R , \quad (36)$$

where this integration is carried out over all space. We now let

$$K = n_1 b_1 + n_2 b_2 + n_3 b_3 , \quad (37)$$

where $b_1$, $b_2$, and $b_3$ are a set of basis vectors in the reciprocal lattice, and $n_1$, $n_2$, and $n_3$ are integers. On substituting the functions $V_1(R)$ and $V_2(R)$ into the integral we obtain

$$C_K = \frac{2\pi e^2}{L^3} \left\{ \frac{2}{k^2 + \alpha^2} + \frac{1}{k^2} \right.$$
$$\left. + (-1)^{n_1+n_2+n_3} \left[ \frac{2}{k^2+\beta^2} - \frac{1}{k^2} \right] \right\} , \quad (38)$$

where $L$ is the shortest distance between positive and negative ions in the crystal. It is to be remembered that

$$k = 2\pi K = 2\pi (n_1 b_1 + n_2 b_2 + n_3 b_3) . \quad (39)$$

Substitution of this expression for $C_K$ into Eq. (33) leaves only the summation over $K$ to be performed.

It is recalled that this value is an approximation to expression (29) wherein we took $E_n$ to be zero. We shall now go back and correct for the first few values of $n$.

From parity considerations it is clear that the integral in expression (29) vanishes when $l$ is even. We therefore need consider only the odd values of $l$ in the correction calculations. This implies immediately that we need not consider $n=1$ for which $l$ has only the value 0. The correction term to be added to (33) is, therefore,

$$4 \sum_K |C_K|^2 \sum_{n=2}^{5} \sum_{\text{odd } l,m} \int \phi_{100}*(r)\phi_{100}(r')\phi_{nlm}(r)\phi_{nlm}*(r')$$
$$\times \sin\left(\frac{k \cdot r}{2}\right) \sin\left(\frac{k \cdot r'}{2}\right) d\tau_{r'} d\tau_r$$
$$\times \left[ \frac{1}{E_1 - E_n - \dfrac{\hbar^2 k^2}{4m}} - \frac{1}{E_1 - \dfrac{\hbar^2 k^2}{4m}} \right] , \quad (40)$$

where the summation over $n$ is terminated at $n=5$.

Consider the sum

$$\sum_{\text{odd } l,m} \int \phi_{100}*(r)\phi_{100}(r')\phi_{nlm}(r)\phi_{nlm}*(r')$$
$$\times \sin\left(\frac{k \cdot r}{2}\right) \sin\left(\frac{k \cdot r'}{2}\right) d\tau_r d\tau_{r'} . \quad (41)$$

We express $\sin(k \cdot r/2)$ in terms of complex exponentials and use the relation

$$e^{ik \cdot r} = \sum_{l'=0}^{\infty} (2l'+1) i^{l'} P_{l'}(\cos\theta) j_{l'}(kr) , \quad (42)$$

where $j_{l'}(kr)$ is a spherical Bessel function. We also write $\phi_{nlm}(r)$ as

$$\phi_{nlm}(r) = R_{nl}(r) Y_l^m(\theta, \phi) . \quad (43)$$

On summation over $m$ and integration over angle, the expression (41) reduces to

$$4\pi \sum_{\text{odd } l} (2l+1) \left[ \int \phi_{100}(r) R_{nl}(r) j_l\left(\frac{kr}{2}\right) r^2 dr \right]^2 . \quad (44)$$

The energy shift given by Eq. (40) therefore reduces to

$$16\pi \sum_K \sum_{n=2}^{5} |C_K|^2 \sum_{\text{odd } l} (2l+1)$$
$$\times \left[ \int \phi_{100}(r) R_{nl}(r) j_l\left(\frac{kr}{2}\right) r^2 dr \right]^2$$
$$\times \left[ \frac{1}{E_1 - E_n - (\hbar^2 k^2/4m)} - \frac{1}{E - (\hbar^2 k^2/4m)} \right] , \quad (45)$$

wherein the integrals can be explicitly evaluated. The summations in expressions (33) and (45) were evaluated on a computer.

These computations yield a second-order energy shift of $-4.51$ eV. Since the unperturbed energy is $-6.802$ eV, this places the energy of the positronium system at $-6.802 - 4.51 = -11.31$ eV.

Since this energy shift is quite large, it was decided to obtain a check on the result by calculating an upper bound to the energy. This was done by evaluating the expected average of the Hamiltonian using the wave function given by the perturbation theory. This perturbed ground-state wave function is given by

$$\psi = \psi_{0,100} + \sum_{knlm} \frac{(\psi_{0,100}, H_1 \psi_{k,nlm})}{E_1 - E_n - (\hbar^2 k^2/4m)} \psi_{k,nlm} . \quad (46)$$

Using this wave function, we wish to calculate $(\psi, H\psi)/$

$(\psi,\psi)$. The numerator reduces to

$$(\psi,H\psi)=E_1+2\sum_{k,nlm}\frac{|(\psi_{0,100},H_1\psi_{k,nlm})|^2}{\left[E_1-E_n-\dfrac{\hbar^2k^2}{4m}\right]}$$

$$=\sum_{k,nlm}\frac{[E_n+(\hbar^2k^2/4m)]|(\psi_{0,100},H_1\psi_{k,nlm})|^2}{[E_1-E_n-(\hbar^2k^2/4m)]^2}. \qquad (47)$$

The denominator reduces to

$$(\psi,\psi)=1+\sum_{k,nlm}\frac{|(\psi_{0,100},H_1\psi_{k,nlm})|^2}{[E_1-E_n-(\hbar^2k^2/4m)]^2}. \qquad (48)$$

The first sum in Eq. (47) is the same as that in expression (24). The other two sums in Eqs. (47) and (48) are evaluated in much the same fashion. The result of this calculation is

$$(\psi,H\psi)/(\psi,\psi)=-13.43\text{ eV}. \qquad (49)$$

It is to be recalled that this is an upper bound to the energy.

It can be shown that the error in the above result, arising from the approximation procedure used in the summations, is less than 0.01 eV. If, in (47) and (48) we attempt to approximate by taking the discrete sum only up to $n=5$, the result obtained for $(\psi,H\psi)/(\psi,\psi)$ is $-7.044$ eV. The large discrepancy between this and the more accurate value obtained above indicates that there is a substantial contribution to the wave function $\psi$ from the higher excited states of positronium. This, in turn, implies (since the $l=0$ states do not contribute) that there is a significant departure of the wave function from spherical symmetry.

## IV. GROUND-STATE ENERGY OF A POSITRON IN THE CRYSTAL

We must now estimate the ground-state energy of a positron in the simulated potential. An upper bound to this energy is calculated by making use of the variational principle. Since we are seeking the ground state, the wave function must have all the symmetries of the potential. A trial wave function $\psi$ is expanded into a Fourier series, where the basis functions have the form

$$\sum_{P(n_1,n_2,n_3)}P(n_1,n_2,n_3)\cos\frac{2\pi n_1X}{a}$$

$$\times\cos\frac{2\pi n_2Y}{a}\cos\frac{2\pi n_3Z}{a}. \qquad (50)$$

The $X$, $Y$, $Z$ coordinates are chosen along the fundamental lattice vectors, each of length $a$. The symbol $P(n_1,n_2,n_3)$ represents a permutation of the three integers $n_1$, $n_2$, and $n_3$. The sum is carried out over all six permutations. This function has the complete symmetry of the potential.

The Fourier coefficients in the expansion of $\psi$ are used as the variable parameters in the variational technique.

The Hamiltonian for the positron is

$$H=-(\hbar^2/2m)\nabla^2+eV(\mathbf{R}), \qquad (51)$$

where $V(\mathbf{R})$ is the crystal potential obtained previously. It can be easily seen that the inner product $(\psi,H\psi)$ is a homogeneous quadratic function of the Fourier coefficients, i.e.,

$$(\psi,H\psi)=\sum_{ij}a_{ij}C_iC_j, \qquad (52)$$

where $C_i$ is a Fourier coefficient and $a_{ij}$ is a constant. Similarly, the inner product $(\psi,\psi)$ has the form

$$(\psi,\psi)=\sum_i b_i^2C_i^2, \qquad (53)$$

where the coefficients $b_i^2$ are constants.

The variational procedure involves minimizing $(\psi,H\psi)$ with respect to the variable parameters. In other words, we wish to minimize $(\psi,H\psi)$ subject to the condition that $(\psi,\psi)=1$. By the introduction of a Lagrange undetermined multiplier this problem reduces to finding the smallest eigenvalue of the matrix whose $(i,j)$th element is $a_{ij}/b_ib_j$. A total of 15 Fourier coefficients were chosen, the corresponding values of $a_{ij}$ and $b_i$ were calculated, and the 15×15 matrix was diagonalized with the aid of a computer.[4] The ground-state energy of the positron was found to be $+7.317$ eV.

## V. POSITRONIUM FORMATION IN THE CRYSTAL

We consider now the energetics of positronium formation following the usual type of argument. Let $E_p$ be the ground-state energy of the bound positronium system in the crystal, $E^+$ the actual energy of the positron, and $E_0^+$ the energy of its ground state, $-V_i$ the energy of an electron at the top of the valence band, and $-V_1$ the energy of an electron at the bottom of the conduction band.

In order for it to be energetically possible for a positron to capture an electron from the valence band to form positronium, the positron energy must be large enough to satisfy the inequality,

$$E^+-V_i\geqslant E_p. \qquad (54)$$

In order for the positronium so formed to persist, energy considerations should forbid the separation of the bound system with the deposition of the electron at the bottom of the conduction band. Thus we require

$$E_0^+-V_1>E^+-V_i. \qquad (55)$$

Values of $V_i$ and $V_1$ for LiH are not available, but for purposes of the present argument it will turn out that rough estimates of these quantities are sufficient. For the alkali halides, $V_i$ ranges up to about 9 eV, and $V_1$ has been estimated of the order of 0.5 eV[5] or less. For use in (54) and (55) we shall set $V_i = 10$ eV and $V_1 = 1$ eV. With the value of $E_p$ obtained in Sec. III, (54) becomes

$$E^+ \geqslant -13.4 + 10 = -3.4 \text{ eV}. \tag{56}$$

This is certainly satisfied even if we set $E^+$ equal to the value of $E_0^+ = 7.3$ eV obtained in Sec. IV.

It can, of course, be argued that the value used for $E_0^+$ is probably much too large, since in obtaining this value the positron was considered as moving in a fixed potential, no regard being taken of polarization effects. In the actual crystal the positron would be expected to concentrate the electron cloud about itself, with a resultant lowering of its energy. The amount by which the energy would thus be lowered would, however, not exceed the free positronium binding energy of 6.8 eV. Making allowance for this, even if we set $E^+ = E_0^+ = 0$ in (55), the inequality is satisfied. Thus, the energy requirement for positronium formation is satisfied for positrons of energies down to the ground-state energy, $E_0^+$.

The inequality (55) can be rewritten

$$E^+ - E_0^+ < V_i - V_1 \sim 9 \text{ eV}, \tag{57}$$

the right-hand side being now the measure of the width of the Ore gap. Thus, we have that a positron in the crystal with an energy anywhere within a range of some 9 eV above the ground-state energy can, by capture of an electron from the valence band, form a positronium-like bound system, which will be energetically stable against dissociation by deposition of the electron in the conduction band.

## VI. DISCUSSION AND CONCLUSIONS

A number of questions arising out of the preceding treatment would seem to merit discussion at this point. These comprise the use of perturbation theory, the perhaps surprisingly low value for the upper bound to the positronium energy, the mean life for electron-positron annihilation from the bound state, and the neglect of exchange in treating the electron and positron of the bound system as being subject to the same effective crystal field.

Perturbation theory is used in the preceding treatment to the extent that it provides a wave function with which to calculate an upper bound to the positronium energy. It is not suggested that this function gives a particularly close approximation to the state of the system. The use of a better function would, however, result in a lower value of the upper bound, and this would strengthen the energetics argument of Sec. V.

For the sake of completeness only, the above wave function is used in Appendix A to estimate the mean life of the positronium system, but obviously no great weight can be attached to the numerical result obtained.

The result obtained in Sec. III for the upper bound to the positronium energy might at first appear to be surprisingly low. It would be expected that the positronium in the crystal would suffer distortion such as to increase its internal energy; and this is indeed the case. However, positronium being an extended system, its constituent electron and positron will not have the same distribution in the crystal, with the result that the two particles may on the average occupy (different) positions of low respective potential energy. It is in fact the very distortion tending to raise the internal energy of the system which enables the positronium to "fit" the shape of the crystal field so as to lower its potential energy. An examination[6] of the expression (49) for the positronium energy reveals a very slow convergence of the series. This indicates the importance of the terms involving large quantum numbers. These higher terms do not greatly affect the internal energy, but through providing high angular momentum components in the wave function they give a distortion of the positronium which results in a large downward shift of the potential energy.

The use of the same form of crystal potential for both particles of the positronium system implies neglect of effects of exchange between the electron of the bound system and electrons in Bloch states of the crystal. An examination of this question, details of which are given in Appendix B, reveals that the exchange energy in the interaction between the electron of the positronium and an electron of the crystal is zero. This constitutes the justification for the neglect of exchange and for the use of the same form of crystal potential for the electron and the positron of the bound system.

The present investigation indicates that positronium formation is probably an important part of the process of positron annihilation in lithium hydride. Pending further investigation, one is tempted to speculate that this might also be the case in other ionic crystals such as other alkali hydrides and alkali halides. If positronium is formed in such a crystal in the triplet state, the subsequent two-photon annihilation of the positron with an electron through a "pick-off" process would be expected to contribute to a $\tau_2$ component of the positron annihilation radiation. Such a $\tau_2$ component has been observed[7] in a number of ionic crystals.

## APPENDIX A: ANNIHILATION MEAN LIFE

For a calculation of the mean annihilation rate from the singlet state of the positronium-like system with

[5] A. J. Dekker, *Solid State Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey), pp. 371–373.

[6] Details of the calculation are given in R. I. Verrall, M.Sc. thesis, University of Manitoba (unpublished).

[7] A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **131**, 1023 (1963).

state function $\psi$ of Eq. (46), it is sufficient to calculate for this state the density of the electron at the location of the positron (averaged over all positions of the center of mass) and compare this with the corresponding density in the ground state of free positronium. The ratio of the two densities will then be equal to the ratio of the corresponding annihilation rates, that of free positronium being known.

It will be recalled that the terms involving excited states of positronium which occur in the expansion (46) all have $l > 0$, and these terms vanish for $\mathbf{r}=0$. Thus, it is only the ground-state term, $\psi_{0,100}$, which contributes to the electron density desired, and the contribution of this term differs from that in free positronium only through the fact that $\psi$ is not normalized to unity. Thus the electron density at the positron for positronium in the crystal is to the corresponding density in the ground state of free positronium in the ratio of $1/(\psi,\psi)=1/1.16$. Thus, for the wave function $\psi$ the mean life of singlet positronium in the crystal is 1.16 times the mean life of singlet, ground-state, free positronium.

### APPENDIX B: EXCHANGE EFFECTS

An examination will now be made of the nature of possible exchange effects, hitherto neglected. For this purpose we consider the system of positronium in the crystal in interaction with an electron in a Bloch state.

Let the wave function for positronium in the crystal be of the form of a superposition of free positronium functions similar to (46), i.e.,

$$\psi(1,2)=\sum A\,(\mathbf{k},nlm)$$
$$\times \exp[\pi i \mathbf{K}\cdot(\mathbf{r}_1+\mathbf{r}_2)]\varphi_{nlm}(\mathbf{r}_1-\mathbf{r}_2), \quad (58)$$

where the subscripts 1 and 2 refer to the positron and electron, respectively. For the electron in the Bloch state we write the wave function (3). For the two systems in interaction we take a symmetrized function

$$\Psi=(1/\sqrt{2})[\psi(1,2)\chi(3)\pm\psi(1,3)\chi(2)]. \quad (59)$$

To examine the effect of exchange, we consider for definiteness the Coulomb interaction between the two electrons. Its average will be proportional to $(\Psi,(1/r_{23})\Psi)$. The direct term in this inner product is equal to

$$\int |\psi(1,2)|^2|\chi(3)|^2\frac{1}{r_{23}}d\tau, \quad (60)$$

while the exchange term is

$$\int \psi^*(1,2)\chi^*(3)\psi(1,3)\chi(2)(1/r_{23})d\tau. \quad (61)$$

In order to compare these two expressions, we select a typical term from the summation which results in each from the substitution of the expansion (58).

Out of the expansion of (60) we take the term

$$I=\int \exp[\pi i(\mathbf{K}'-\mathbf{K})\cdot(\mathbf{r}_1+\mathbf{r}_2)]\varphi_{nlm}^*(\mathbf{r}_1-\mathbf{r}_2)$$
$$\times \varphi_{n'l'm'}(\mathbf{r}_1-\mathbf{r}_2)|\chi(\mathbf{r}_3)|^2d\tau. \quad (62)$$

By a coordinate transformation this can be rewritten

$$I=\int \exp[\pi i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}_1]\varphi_{nlm}^*(\mathbf{r}_1)\varphi_{n'l'm'}(\mathbf{r}_1)d\tau_1$$
$$\times \int \exp[2\pi i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}_2]\frac{1}{r_2}d\tau_2$$
$$\times \int |\chi(\mathbf{r}_3)|^2 \exp[2\pi i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}_3]d\tau_3. \quad (63)$$

Out of (61) we take the corresponding term

$$J=\int \exp[\pi i\{\mathbf{K}'\cdot(\mathbf{r}_1+\mathbf{r}_3)-\mathbf{K}\cdot(\mathbf{r}_1+\mathbf{r}_2)\}]\varphi_{nlm}^*(\mathbf{r}_1-\mathbf{r}_2)$$
$$\times \varphi_{n'l'm'}(\mathbf{r}_1-\mathbf{r}_3)\chi(\mathbf{r}_3)\chi(\mathbf{r}_2)d\tau. \quad (64)$$

We can, by omitting the exponentials in (64), write

$$|J|\leqslant \int \varphi_{nlm}^*(\mathbf{r}_1-\mathbf{r}_2)\varphi_{n'l'm'}(\mathbf{r}_1-\mathbf{r}_3)$$
$$\times \chi^*(\mathbf{r}_3)\chi(\mathbf{r}_2)\frac{1}{r_{23}}d\tau. \quad (65)$$

Because of the nature of the positronium functions $\varphi$ the integral (65) converges, in spite of $\chi$ not being quadratically integrable. By contrast, the third integral in (63) diverges. Thus, a suitable box normalization to ensure the convergence of the direct interaction term $I$ causes the exchange term $J$ to vanish.