Lattice vibrations induced by a polarizable impurity atom in polar crystals

J. Mahanty* and V. V. Paranjape†
Research School of Physical Sciences, The Australian National University, Caberra, ACT.2600, Australia
(Received 19 March 1974)

The effect of a polarizable impurity atom on the frequency of optical vibrations of a crystal is calculated. The impurity-lattice interaction is treated by considering the lattice polarization as discrete in contrast to earlier methods based on the continuum approximation. In the appropriate limit, our result goes over exactly to the result of the continuum theory.

I. INTRODUCTION

Dean, Manchon, and Hopfield[1] have recently observed lattice modes bound to neutral impurities in GaP. These modes are shown to be due to the coupling between the impurity atom and the optical modes of the host lattice. Using an appropriate form of the Fröhlich Hamiltonian they have calculated the energies associated with these modes, which are in reasonable agreement with experimental data. Implicit in these calculations is the assumption of a continuous polarization field of the lattice. For an impurity whose electronic wave function extends over several lattice cells this assumption is reasonable, but for a strongly localized impurity state the discreteness of the lattice may be important and ought to be taken into account. The purpose of this paper is to analyze the problem within the framework of a model that retains the discrete features of the lattice. The energy of the local modes calculated through this model is a generalization of the analysis given by Dean *et al.*[1] and goes over to their value in the continuum limit. The effect of dispersion of the optical modes is included in this model. The value of the change in the binding energy of the impurity electron due to electron-phonon coupling with the optical mode is also computed.

The optical modes in a polar crystal can be considered as arising out of the dipolar oscillations in different lattice cells. This coupling is rather weak and hence the dispersion in the optical branch is rather small. Although this picture of optical modes is not as rigorous as what one uses in the full lattice dynamical analysis of the vibrations, it is adequate to bring out the essential physics of the present problem, and will be the principal feature of the model of the polar crystal adopted in this paper.

In the presence of the impurity additional coupling between the dipolar oscillators in different lattice cells arises through the induced polarization of the impurity. This coupling perturbs the optical modes and can produce local modes of the sort observed by Dean *et al.*[1] We shall examine this in detail.

II. ANALYSIS OF THE MODEL

The equation of motion for the effective displacement $\vec{u}_{\vec{l}}$ which leads to polarization within the $\vec{l}$th cell of the crystal with a single impurity is

$$-\mu\omega^2\vec{u}_{\vec{l}} = \sum_{\vec{l}'} \vec{F}(|\vec{l}-\vec{l}'|)\cdot\vec{u}_{\vec{l}'} + \sum_{\vec{l}'} \vec{D}(\vec{l},\vec{l}')\cdot\vec{u}_{\vec{l}'}\,, \tag{2.1}$$

where μ is the effective mass associated with the dipolar oscillations within each cell, $\vec{F}(|\vec{l}-\vec{l}'|)$ and $\vec{D}(\vec{l},\vec{l}')$ are the force-constant tensors, giving the force on the $\vec{l}$th dipole due to the $\vec{l}'$th dipole through direct interaction and via the impurity, respectively. $\vec{F}(|\vec{l}-\vec{l}'|)$ depends on the difference $|\vec{l}-\vec{l}'|$, due to lattice translation symmetry, whereas $\vec{D}(\vec{l},\vec{l}')$ depends on $\vec{l}$ and $\vec{l}'$ separately, as also on the position of the impurity. We shall treat the impurity term in (2.1) as a perturbation.

In terms of the Fourier transforms $\vec{v}(\vec{k})$ of $\vec{u}_{\vec{l}}$ defined through the equations

$$\vec{u}_{\vec{l}} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{l}}\,\vec{v}(\vec{k})$$

and

$$\vec{v}(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{\vec{l}} \vec{u}_{\vec{l}}\, e^{i\vec{k}\cdot\vec{l}}\,, \tag{2.2}$$

where N is the number of cells and $\vec{k}$ is a wave vector defined within the Brillouin zone, Eq. (2.1) can be written as

$$-\mu[\omega^2 - \omega^2(\vec{k})]\vec{v}(\vec{k}) = \sum_{\vec{k}'} \vec{D}(\vec{k},\vec{k}')\vec{v}(\vec{k}')\,. \tag{2.3}$$

Here, for simplicity, we presume that $\vec{F}$ is isotropic and

$$\mu\omega^2(\vec{k}) = \sum_{\vec{l}} e^{-i\vec{k}\cdot\vec{l}}\,F(|\vec{l}|)\,, \tag{2.4}$$

$$\vec{D}(\vec{k},\vec{k}') = \frac{1}{N}\sum_{\vec{l},\vec{l}'} \vec{D}(\vec{l},\vec{l}')e^{-i(\vec{k}\cdot\vec{l}-\vec{k}'\cdot\vec{l}')}. \tag{2.5}$$

We shall see in Sec. III that $\vec{D}(\vec{l},\vec{l}')$ can be written as a sum of separable factors in the form

$$\vec{D}(\vec{l},\vec{l}') = \alpha[\vec{G}^T(\vec{l})\vec{G}(\vec{l}')+\vec{H}^T(\vec{l})\vec{H}(\vec{l}')+\cdots], \tag{2.6}$$

where T stands for transposed matrix. The various terms in the right-hand side of Eq. (2.6) correspond to the different electronic transitions of the impurity atom occurring in its polarizability. We shall retain only two terms, taking a hydrogenic model for the impurity atom, corresponding to transitions $1s \rightarrow 2s$ and $1s \rightarrow 2p$. We can then write (2.3) in the form

$$-\mu[\omega^2-\omega^2(\vec{k})]\vec{v}(\vec{k}) = \alpha\sum_{\vec{k}'}[\vec{G}^*(\vec{k})\vec{G}(\vec{k}') + \vec{H}^*(\vec{k})\vec{H}(\vec{k}')]\vec{v}(\vec{k}'), \tag{2.7}$$

where

$$\vec{G}(\vec{k})\{\text{or } \vec{H}(\vec{k})\} = \frac{1}{\sqrt{N}}\sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}}\,\vec{G}(\vec{l})\{\text{or } \vec{H}(\vec{l})\}. \tag{2.8}$$

In (2.7), $\omega(\vec{k})$ is the frequency of the longitudinal-optical (LO) modes of the lattice without the impurity atom. The other modes would not produce as strong an interaction with the impurity as the LO mode, and will not occur in this model. Multiplying Eq. (2.7) by $\vec{G}(\vec{k})$ {and $\vec{H}(\vec{k})$} and summing both sides over $\vec{k}$, we get the secular equation

$$\begin{vmatrix} \vec{I}-\frac{\alpha}{\mu}\sum_{\vec{k}}\frac{\vec{G}(\vec{k})\vec{G}^*(\vec{k})}{\omega^2(\vec{k})-\omega^2} & -\frac{\alpha}{\mu}\sum_{\vec{k}}\frac{\vec{G}(\vec{k})\vec{H}^*(\vec{k})}{\omega^2(\vec{k})-\omega^2} \\ -\frac{\alpha}{\mu}\sum_{\vec{k}}\frac{\vec{H}(\vec{k})\vec{G}^*(\vec{k})}{\omega^2(\vec{k})-\omega^2} & \vec{I}-\frac{\alpha}{\mu}\sum_{\vec{k}}\frac{\vec{H}(\vec{k})\vec{H}^*(\vec{k})}{\omega^2(\vec{k})-\omega^2} \end{vmatrix} = 0. \tag{2.9}$$

Here $\vec{I}$ is the unit tensor. The roots of this secular determinant would give us the perturbed LO frequencies of the lattice.

III. ANALYSIS OF THE LATTICE-IMPURITY INTERACTION

An explicit form of the term $\vec{D}(\vec{l},\vec{l}')$ can be obtained as follows. The change in the energy of the crystal due to the coupling of the dipoles through the induced polarization of the impurity can be written as

$$\Delta E = \tfrac{1}{2}\sum_{\vec{l},\vec{l}'} \vec{u}_{\vec{l}}\cdot\vec{D}(\vec{l},\vec{l}')\cdot\vec{u}_{\vec{l}'}. \tag{3.1}$$

This energy can be evaluated by considering the polarization induced on the impurity due to a dipole $(q\vec{u}_{\vec{l}})$ at $\vec{l}$, calculating the energy of a dipole $(q\vec{u}_{\vec{l}'})$ at $\vec{l}'$ in the field produced by the polarized impurity, and summing over all lattice sites. Here q is the effective charge of the dipole in a lattice cell. The induced polarization on the impurity can be calculated from the potential energy of the impurity electron (with the impurity core located at the origin) due to the dipole in the $\vec{l}$th cell:

$$V(\vec{l}) = -\frac{eq\vec{u}_{\vec{l}}\cdot(\vec{r}-\vec{R}_{\vec{l}})}{\epsilon_\infty|\vec{r}-\vec{R}_{\vec{l}}|^3}, \tag{3.2}$$

where ϵ_∞ is the high-frequency dielectric constant, $\vec{r}$ is the electronic coordinate, and $\vec{R}_{\vec{l}}$ the coordinate of the $\vec{l}$th cell. If we assume that $\vec{u}_{\vec{l}}$ oscillates with frequency ω, compute the induced polarization on the impurity by second-order time-dependent perturbation theory, evaluate the potential energy of the dipole $(q\vec{u}_{\vec{l}'})$ due to the induced polarization, and sum over all cells, we get

$$\Delta E = \sum_{\vec{l},\vec{l}',n}\frac{\langle 1s|V(\vec{l})|n\rangle\langle n|V(\vec{l}')|1s\rangle[E_n-E_{1s}]}{(E_n-E_{1s})^2-(\hbar\omega)^2}. \tag{3.3}$$

If we retain only two terms, $n=2s$ and $n=2p$ in (3.3), we get ΔE in essentially the form of (3.1), and $\vec{D}(\vec{l},\vec{l}')$ is thus determined. The details of the calculation are given in Appendix A and the results are

$$\vec{G}^T(\vec{l}) = \begin{bmatrix} A(\vec{l}) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$\vec{H}^T(\vec{l}) = \begin{bmatrix} B(\vec{l})\cos\theta_{\vec{l}} & B(\vec{l})\sin\theta_{\vec{l}}\cos\phi_{\vec{l}} & B(\vec{l})\sin\theta_{\vec{l}}\sin\phi_{\vec{l}} \\ -C(\vec{l})\sin\theta_{\vec{l}} & C(\vec{l})\cos\theta_{\vec{l}}\cos\phi_{\vec{l}} & C(\vec{l})\cos\theta_{\vec{l}}\sin\phi_{\vec{l}} \\ 0 & -C(\vec{l})\sin\phi_{\vec{l}} & C(\vec{l})\cos\phi_{\vec{l}} \end{bmatrix}, \qquad \alpha(\omega) = \frac{2(E_2-E_{1s})}{(E_2-E_{1s})^2-(\hbar\omega)^2}, \tag{3.4}$$

where

$$A(\vec{l}) = \frac{-4}{9(2)^{1/2}} \left(\frac{-eq}{\epsilon_\infty a_0^2}\right) \left(\frac{3R_{\vec{l}}}{2a_0}\right) e^{-3R_{\vec{l}}/2a_0} ,$$

$$B(\vec{l}) = \frac{4}{27(2)^{1/2}} \left(\frac{-eq}{\epsilon_\infty a_0^2}\right) \left\{ e^{-3R_{\vec{l}}/2a_0} \left[48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 + 48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^2 + 24\left(\frac{2a_0}{3R_{\vec{l}}}\right) + 9 + 3\left(\frac{3R_{\vec{l}}}{2a_0}\right) \right] - 48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 \right\} ,$$

$$C(\vec{l}) = \frac{4}{9(2)^{1/2}} \left(\frac{-eq}{\epsilon_\infty a_0^2}\right) \left\{ e^{-3R_{\vec{l}}/2a_0} \left[-8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 - 8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^2 - 4\left(\frac{2a_0}{3R_{\vec{l}}}\right) - 1 \right] + 8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 \right\} . \quad (3.5)$$

Here a_0 is the effective Bohr radius of the impurity atom, and $R_{\vec{l}}$, $\theta_{\vec{l}}$, and $\phi_{\vec{l}}$ are the polar coordinates of the $\vec{l}$th dipole. Equations (3.4) and (3.5) when used in (2.6), (2.8), and (2.9) give us the explicit form of the elements of the secular determinant.

IV. FREQUENCIES OF THE LOCAL MODES

The frequencies of the local modes are obtained from the roots of (2.9) which are outside the range of values of $\omega(k)$. An approximate formula can be obtained if the dispersion in the LO branch is ignored. Then, in a cubic crystal for instance, the off-diagonal terms in the matrices such as

$$\sum_{\vec{k}} \vec{G}(\vec{k})\vec{H}^*(\vec{k}) , \quad \sum_{\vec{k}} \vec{H}(\vec{k})\vec{G}^*(\vec{k})$$

vanish, and if the shift from the unperturbed LO frequency ω_0 is sufficiently small so that in (3.4) ω_0 can be written for ω, the roots of (2.9) are

$$\omega^2 = \omega_0^2 - \frac{\alpha(\omega_0)}{\mu} \sum_{\vec{l}} A^2(\vec{l}) , \quad (4.1)$$

$$\omega^2 = \omega_0^2 - \frac{\alpha(\omega_0)}{\mu} \sum_{\vec{l}} [B^2(\vec{l}) \cos^2\theta_{\vec{l}} + C^2(\vec{l}) \sin^2\theta_{\vec{l}}] , \quad (4.2)$$

$$\omega^2 = \omega_0^2 - \frac{\alpha(\omega_0)}{\mu} \sum_{\vec{l}} [B^2(\vec{l}) \sin^2\theta_{\vec{l}} \sin^2\phi_{\vec{l}} + C^2(\vec{l}) (\cos^2\theta_{\vec{l}} \sin^2\phi_{\vec{l}} + \cos^2\phi_{\vec{l}})] . \quad (4.3)$$

The effect of dispersion of the LO branch can, in principle, be taken into consideration by performing the $\vec{k}$ sum in (2.9) with $\omega^2(\vec{k})$ being used in it instead of ω_0. If the dispersion is small and can be approximated by a nearest-neighbor-type interaction in a cubic crystal, i.e.,

$$\omega^2(\vec{k}) = \omega_0^2[1 + \beta(\cos k_x a + \cos k_y a + \cos k_z a)] ,$$

where a is the length of the cubic cell of the lattice and $\beta \ll 1$, it is not difficult to show that the local-mode frequencies will shift from their values in (4.1)–(4.3) by about $\beta\omega_0$. We shall not dwell on this dispersion aspect in any more detail, in view of the relatively small dispersions in LO branches in actual crystals.

V. APPLICATIONS OF THE MODEL

We shall examine here the applicability of this model to two situations—one in which the wave function of the impurity atom is strongly localized and the other in which it is spread over several lattice cells.

A. Strongly bound states

When the wave function is strongly localized the sum over $\vec{l}$ in Eqs. (4.1)–(4.3) reduce essentially to that over the nearest neighbor of the impurity. With this approximation and using (3.5) we can write Eq. (4.1) in the form

$$\omega = \omega_0 - \frac{4}{3} \frac{E_{2s} - E_{1s}}{(E_{2s} - E_{1s})^2 - (\hbar\omega_0)^2} \frac{e^2q^2a^2}{\epsilon_\infty^2 a_0^6 \mu\omega_0} e^{-3a/a_0} . \quad (5.1)$$

Similar expressions can be obtained for (4.2) and (4.3). Equation (5.1) may be written in terms of the static dielectric constant ϵ_0 of the material if we make use of the well known Born result[2]

$$\epsilon_0 = \epsilon_\infty + 4\pi Nq^2/\omega_T^2\mu , \quad (5.2)$$

where ω_T is the transverse mode frequency, and is related to ω_0 by

$$\left(\frac{\omega_T}{\omega_0}\right)^2 = \frac{\epsilon_\infty}{\epsilon_0} . \quad (5.3)$$

The quantity N in (5.2) is the density of lattice cells. Equation (5.1), using (5.2) and (5.3), may now be written as

$$\omega = \omega_0 - \frac{\omega_0}{3\pi} \left[\frac{E_{2s} - E_{1s}}{(E_{2s} - E_{1s})^2 - (\hbar\omega_0)^2}\right] \left(\frac{e^2}{a_0}\right) \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \times \left(\frac{a}{a_0}\right)^5 e^{-3a/a_0} . \quad (5.4)$$

It follows from (5.4) that in the limit $a_0 \to 0$ the shift in the frequency vanishes as is expected.

B. Weakly bound states

If the electron wave function of the impurity is spread out over a large number of cells of the host crystal, the sums in (4.1)–(4.3) can be replaced by integrations so that

$$\sum_{\vec{l}} = N \int R_{\vec{l}}^2 \sin\theta_{\vec{l}}\, dR_{\vec{l}}\, d\theta_{\vec{l}}\, d\phi_{\vec{l}} . \tag{5.5}$$

Using (3.5) and (5.5) we may express (4.1) as

$$\omega^2 = \omega_0^2 - \tfrac{16}{729} 4\pi N \frac{\alpha(\omega_0)}{\mu} \frac{e^2 q^2}{\epsilon_\infty^2 a_0} . \tag{5.6}$$

Similar expressions for (4.2) and (4.3) can also be obtained. Using (5.2) and (5.3) we may now write Eq. (5.6) in the following form:

$$\omega = \omega_0 - \tfrac{16}{729} \left(\frac{E_{2s} - E_{1s}}{(E_{2s} - E_{1s})^2 - (\hbar\omega_0)^2} \right) \left(\frac{e^2}{a_0} \right) \times \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \omega_0 . \tag{5.7}$$

The equation (5.7) agrees exactly with the result of Ref. 1.

C. Binding energy of the impurity

If we combine shifts in the lattice frequencies, we obtain the total shift in the zero-point energy of the lattice. This may be equated to a change in the binding energy of the impurity atom. The details of such a calculation are not attempted in this paper. It is not difficult to see, however, that the form of the expression for the change in the binding energy ΔE can be written as

$$\Delta E = -\frac{e^2 q^2 \hbar}{\epsilon_\infty^2 a_0^4 \mu \omega_0} \alpha(\omega_0) J\left(\frac{a}{a_0} \right) , \tag{5.8}$$

where the function

$$J\left(\frac{a}{a_0} \right) \to 0 \quad \text{in the limit } a_0 \to 0 ,$$

while

$$J\left(\frac{a}{a_0} \right) \to \left(\frac{a_0}{a} \right)^3 \quad \text{in the limit } a_0 \gg a$$

$$\text{provided } a_0 < (e^2/\hbar\omega_0) . \tag{5.9}$$

A change in the energy of a weakly bound impurity is treated by several authors,[3,4] while the present model provides a method to obtain ΔE for strongly bound impurity states.

ACKNOWLEDGMENTS

One of the authors (V. V. P.) would like to thank Professor K. J. LeCouteur for his hospitality at The Australian National University, and the National Research Council of Canada for their support.

APPENDIX A

Here we shall evaluate (3.3) for $n = 2s$ and $n = 2p$ and compare the result with (2.6) and (3.1) to give explicit expressions for $\vec{G}^T(\vec{l})$ and $\vec{H}^T(\vec{l})$. The wave functions to be used in (3.3) are

$$|1s\rangle = \frac{1}{(\pi)^{1/2}} \frac{1}{(a_0)^{3/2}} e^{-r/a_0} , \tag{A1}$$

$$|2s\rangle = \frac{1}{(\pi)^{1/2}} \frac{1}{2} \frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} , \tag{A2}$$

$$|2p_{0,\pm1}\rangle = \frac{1}{(\pi)^{1/2}} \frac{1}{2(2a_0)^{3/2}} \left(\frac{r}{a_0} \right) e^{-r/2a_0} \times \begin{Bmatrix} \cos\theta & \text{for } p_0 \\ \sin\theta\cos\phi & \text{for } p_{+1} \\ \sin\theta\sin\phi & \text{for } p_{-1} \end{Bmatrix} , \tag{A3}$$

where r, θ, ϕ are the electron position coordinates for a given system of coordinates.

The potential energy $V(\vec{l})$ in (3.1) may be written as

$$V(\vec{l}) = -\frac{eq}{\epsilon_\infty} \left[\frac{\vec{u}^{R\vec{l}}(r\cos\theta' - R_{\vec{l}}) + \vec{u}^{\theta\vec{l}}(r\sin\theta'\cos\phi') + \vec{u}^{\phi\vec{l}}(r\sin\theta'\sin\phi)}{(r^2 + R_{\vec{l}}^2 - 2rR_{\vec{l}}\cos\theta')^{3/2}} \right] , \tag{A4}$$

where $\vec{u}^{R\vec{l}}$, $\vec{u}^{\theta\vec{l}}$, $\vec{u}^{\phi\vec{l}}$ are the three components of $\vec{u}_{\vec{l}}$ in the direction of increasing $R_{\vec{l}}$, $\theta_{\vec{l}}$, and $\phi_{\vec{l}}$ and θ', ϕ' are the angles defined so that the projections of $\vec{r}$ in the directions $u^{R\vec{l}}$, $u^{\theta\vec{l}}$, $u^{\phi\vec{l}}$ are, respectively, $r\cos\theta'$, $r\sin\theta'\cos\phi'$, $r\sin\theta'\sin\phi'$. The matrix element $\langle 1s|\, V(\vec{l})\, |2s\rangle$ may be evaluated using (A1), (A2), and (A4) to give, in matrix notation,

$$\langle 1s|\, V(\vec{l})\, |2s\rangle = [u^{R\vec{l}}, u^{\theta\vec{l}}, u^{\phi\vec{l}}] \begin{bmatrix} A(\vec{l}) \\ 0 \\ 0 \end{bmatrix} , \tag{A5}$$

where

$$A(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty} \right) \langle 1s| \frac{(r\cos\theta - R_{\vec{l}})}{(r^2 + R_{\vec{l}}^2 - 2rR_{\vec{l}}\cos\theta)^{3/2}} |2s\rangle . \tag{A6}$$

Substituting (A5) into (3.3) and considering $n = 2s$ only we may write by comparison with (2.6) and (3.1) the result

$$\vec{G}^T(\vec{l}) = \begin{bmatrix} A(\vec{l}) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{A7}$$

and

$$\alpha = \frac{2(E_{2s} - E_{1s})}{(E_{2s} - E_{1s})^2 - (\hbar\omega)^2} \,. \tag{A8}$$

In the matrix element $\langle 1s | V(\vec{1}) | 2p\rangle$, the potential energy $V(\vec{1})$ is expressed in terms of angles θ' and ϕ' while the state $|2p\rangle$ is given in angles θ and ϕ. The two sets of angles are related to each other through

$$\begin{bmatrix} r\cos\theta \\ r\sin\theta\cos\phi \\ r\sin\theta\sin\phi \end{bmatrix} = \begin{bmatrix} \cos\theta_{\vec{1}} & -\sin\theta_{\vec{1}} & 0 \\ \sin\theta_{\vec{1}}\cos\phi_{\vec{1}} & \cos\theta_{\vec{1}}\cos\phi_{\vec{1}} & -\sin\phi_{\vec{1}} \\ \sin\theta_{\vec{1}}\sin\phi_{\vec{1}} & \cos\theta_{\vec{1}}\sin\phi_{\vec{1}} & \cos\phi_{\vec{1}} \end{bmatrix} \begin{bmatrix} r\cos\theta' \\ r\sin\theta'\cos\phi' \\ r\sin\theta'\sin\phi' \end{bmatrix} \,, \tag{A9}$$

where the elements of the tensor are the cosines of angles between directions of $u^{R\vec{1}}$, $u^{\theta\vec{1}}$, $u^{\phi\vec{1}}$ and Cartesian coordinates defining angles θ and ϕ. We may now use (A1), (A3), (A4), and (A9) to write in matrix notation the following results:

$$\begin{aligned}
\langle 1s | V(\vec{1}) | 2p_0\rangle &= [u^{R\vec{1}}, u^{\theta\vec{1}}, u^{\phi\vec{1}}] \begin{bmatrix} B(\vec{1})\cos\theta_{\vec{1}} \\ -C(\vec{1})\sin\theta_{\vec{1}} \\ 0 \end{bmatrix} \,, \\
\langle 1s | V(\vec{1}) | 2p_1\rangle &= [u^{R\vec{1}}, u^{\theta\vec{1}}, u^{\phi\vec{1}}] \begin{bmatrix} B(\vec{1})\sin\theta_{\vec{1}}\cos\phi_{\vec{1}} \\ C(\vec{1})\cos\theta_{\vec{1}}\cos\phi_{\vec{1}} \\ -C(\vec{1})\sin\phi_{\vec{1}} \end{bmatrix} \,, \\
\langle 1s | V(\vec{1}) | 2p_{-1}\rangle &= [u^{R\vec{1}}, u^{\theta\vec{1}}, u^{\phi\vec{1}}] \begin{bmatrix} B(\vec{1})\sin\theta_{\vec{1}}\sin\phi_{\vec{1}} \\ C(\vec{1})\cos\theta_{\vec{1}}\sin\phi_{\vec{1}} \\ C(\vec{1})\cos\phi_{\vec{1}} \end{bmatrix} \,,
\end{aligned} \tag{A10}$$

where

$$B(\vec{1}) = \frac{-eq}{\epsilon_\infty} \langle 1s | \frac{r\cos\theta - R_{\vec{1}}}{(r^2 + R_{\vec{1}}^2 - 2rR_{\vec{1}}\cos\theta)^{3/2}} | 2p_0\rangle \,, \tag{A11}$$

$$C(\vec{1}) = \frac{-eq}{\epsilon_\infty} \langle 1s | \frac{r\sin\theta(\cos\phi \text{ or } \sin\phi)}{(r^2 + R_{\vec{1}}^2 - 2rR_{\vec{1}}\cos\theta)^{3/2}} | 2p_{+1} \text{ or } 2p_{-1}\rangle \,. \tag{A12}$$

Substituting (A10) into (3.3) and considering the $n = 2p$ term only, we are able to write by comparison with the result (2.6) and (3.1), $\vec{\vec{H}}^T$ in the following form:

$$\vec{\vec{H}}^T(\vec{1}) = \begin{bmatrix} B(\vec{1})\cos\theta_{\vec{1}} & B(\vec{1})\sin\theta_{\vec{1}}\cos\phi_{\vec{1}} & B(\vec{1})\sin\theta_{\vec{1}}\sin\phi_{\vec{1}} \\ (-)C(\vec{1})\sin\theta_{\vec{1}} & C(\vec{1})\cos\theta_{\vec{1}}\cos\phi_{\vec{1}} & C(\vec{1})\cos\theta_{\vec{1}}\sin\phi_{\vec{1}} \\ 0 & (-)C(\vec{1})\sin\phi_{\vec{1}} & C(\vec{1})\cos\phi_{\vec{1}} \end{bmatrix} \,, \tag{A13}$$

with

$$\alpha = \frac{2(E_{2p} - E_{1s})}{(E_{2p} - E_{1s})^2 - (\hbar\omega)^2} \,.$$

APPENDIX B

Here we shall give relevant steps in the evaluation of $A(\vec{1})$, $B(\vec{1})$, $C(\vec{1})$. Consider

$$A(\vec{1}) = \left(\frac{-eq}{\epsilon_\infty}\right) \int \frac{1}{\pi a_0^3 (2)^{5/2}} \left(2 - \frac{r}{a_0}\right) e^{-3r/2a_0} \frac{(r\cos\theta - R_{\vec{1}})}{(r^2 + R_{\vec{1}}^2 - 2rR_{\vec{1}}\cos\theta)^{3/2}} r^2 dr \sin\theta \, d\theta \, d\phi \,. \tag{B1}$$

Integration over ϕ gives 2π. Performing the θ integration, we then obtain

$$A(\vec{l}) = \left(\frac{eq}{\epsilon_\infty}\right) \frac{4}{(2a_0^2)^{3/2}} \frac{1}{R_{\vec{l}}^2} \int_0^{R_{\vec{l}}} \left(1 - \frac{r}{2a_0}\right) e^{-3r/2a_0} r^2 \, dr ,$$

which on r integration leads to

$$A(\vec{l}) = \left(\frac{-eq}{a_0^2 \epsilon_\infty}\right) \left(\frac{-4}{5(2)^{1/2}}\right) \left(\frac{3R_{\vec{l}}}{2a_0}\right) e^{-3R_{\vec{l}}/2a_0} . \tag{B2}$$

The expression for $B(\vec{l})$ can be written as

$$B(\vec{l}) = \int\int\int \frac{1}{2\pi(2a_0)^{3/2}} \left(\frac{r}{a_0}\right) \frac{\cos\theta(r\cos\theta - R_{\vec{l}})}{(r^2 + R_{\vec{l}}^2 - 2rR_{\vec{l}}\cos\theta)^{3/2}} e^{-3r/2a_0} r^2 \sin\theta \, dr \, d\theta \, d\phi .$$

Integrating over the angles gives

$$B(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty}\right) \frac{1}{3(2)^{1/2} a_0^4} \left[-\frac{2}{R_{\vec{l}}^3} \int_0^{R_{\vec{l}}} e^{-3r/2a_0} r^4 \, dr + \int_{R_{\vec{l}}}^{\infty} e^{-3r/2a_0} r \, dr \right]$$

and r integration produces

$$B(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty a_0^2}\right) \left(\frac{4}{27(2)^{1/2}}\right) \left\{ e^{-3R_{\vec{l}}/2a_0} \left[48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 + 48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^2 + 24\left(\frac{2a_0}{3R_{\vec{l}}}\right) + 9 + 3\left(\frac{3R_{\vec{l}}}{2a_0}\right) \right] - 48\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 \right\} . \tag{B3}$$

Finally we write

$$C(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty}\right) \int\int\int \frac{1}{2\pi(2a_0^2)^{3/2}} \left(\frac{r^2}{a_0}\right) \frac{\sin^2\theta \sin^2\phi}{(r^2 + R_{\vec{l}}^2 - 2rR_{\vec{l}}\cos\theta)^{3/2}} r^2 \sin\theta \, dr \, d\theta \, d\phi .$$

Integration over the angles gives

$$C(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty}\right) \frac{1}{3(2)^{1/2} a_0^4} \left[\frac{1}{R_{\vec{l}}^3} \int_0^{R_{\vec{l}}} e^{-3r/2a_0} r^4 \, dr + \int_{R_{\vec{l}}}^{\infty} e^{-3r/2a_0} r \, dr \right]$$

and the integration over r yields

$$C(\vec{l}) = \left(\frac{-eq}{\epsilon_\infty a_0^2}\right) \frac{4}{9(2)^{1/2}} \left\{ e^{-3r/2a_0} \left[-8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 - 8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^2 - 4\left(\frac{2a_0}{3}\right) - 1 \right] + 8\left(\frac{2a_0}{3R_{\vec{l}}}\right)^3 \right\} . \tag{B4}$$

---

*On leave from Department of Physics, Indian Institute of Technology, Kanpur 16 (U.P.), India.
†On leave from Department of Physics, Lakehead University, Thunder Bay, Ontario, Canada.

[1]P. J. Dean, D. D. Manchon, Jr., and J. J. Hopfield, Phys. Rev. Lett. 25, 1027 (1970).
[2]B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).
[3]P. M. Platzman, Phys. Rev. 125, 1061 (1962).
[4]J. Sak, Phys. Rev. B 3, 3356 (1971).