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Electronic-structure determination of light-impurity–phonon interaction in solids

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A model is discussed in which a solid is simulated by a quantum-mechanical molecular cluster of atoms embedded in a classical atomistic crystal. An effective crystal Hamiltonian is derived, based on adiabatic and harmonic approximations. The relationship is demonstrated between the cluster state and perfect crystal equilibrium configuration and force constants. Similarly, when an impurity is introduced, the relationship is found between the cluster state and the linear and quadratic impurity-phonon coupling coefficients. Also, the effective potential is found for the quantum-mechanical treatment of a light impurity not subject to the harmonic approximation. The distortion field and force constants of the defect crystal containing the impurity are discussed. The results are related to practical methods of computation. The relationship of this work to the problem of quantum diffusion of muonium in alkali halides is described.

I. INTRODUCTION

Theoretical analysis and computer simulation of a point defect in a solid are commonly based on a model consisting of a cluster of atoms, including the defect, whose electrons are treated quantum mechanically, with the cluster embedded in a crystal composed of classical atoms.[1] Attention is given to the problem of interfacing the quantum and classical regions in a consistent way. Usually the nuclei or atomic cores of cluster atoms and the embedding classical atoms are treated statically. Sometimes the entire system is relaxed to mechanical equilibrium, allowing one to analyze defect processes at absolute zero of temperature by comparing total energies of different configurations of the defect. Examples are optical transitions[2] and classical diffusion activation.[3]

For many systems and processes the static lattice approximation is inappropriate, but the harmonic approximation may be valid for the crystal vibrations, which are described by quantum-mechanical phonons. For light impurities, such as muonium, hydrogen, and possibly others, the harmonic approximation may not apply to the impurity itself, and its nucleus must be treated quantum mechanically. The motivation for this work was a study of diffusion of muonium in alkali halides, for which experimental results are available.[4] The application of the present results to muonium in the tight-binding approximation[5] has been studied separately.[6] However, because of the variety of systems and processes to which the method applies, and the different approximations that may be considered, it is worthwhile to present the derivation in a general form.

In Sec. II we derive the effective phonon Hamiltonian for a perfect crystal part of which is described by an embedded quantum cluster, with the remainder, the embedding region, based on point-mass atoms. This provides explicit relationships between the state function of the static embedded cluster and the lattice spacing and phonon dispersion relations. In Sec. III we derive the Hamiltonian for light-impurity–phonon interaction, explicitly adapted to the embedded quantum cluster model. The form of the derived results turns out to be relatively simple from the viewpoints of both physical interpretation and numerical evaluation. The formalism will be seen to apply to all classes of materials for which reliable atomistic models exist. In this work an atomistic model consists of point mass atoms interacting with pairwise potentials. The atoms may be charged point ions. In the Appendix we extend the results to include the shell model for ionic crystals.[7] In Sec. IV we summarize our results.

II. THE PERFECT CRYSTAL

We first write down the Hamiltonian for the crystal in the absence of the impurity. A superscript (0) will be used to denote entities that relate to this perfect crystal, which consists of a quantum cluster of atoms embedded in an infinite crystal of point-mass ions. It is assumed that the cluster and its embedding region are physically consistent, so that combined they represent the experimental properties of the material. The cluster will contain the site at which an impurity will later be introduced, and it will also contain all atoms whose electronic structure will be significantly affected by the defect, and all atoms which, in the presence of the defect, have equilibrium displacements from perfect crystal positions that are beyond the harmonic approximation. We now proceed to derive the effective Hamiltonian for the perfect crystal, based on the adiabatic approximation for electrons of the cluster, and the harmonic approximation for ionic motions.

This perfect crystal Hamiltonian is

$$H^{(0)}=(H_e^{(0)}+H_L)\ , \tag{2.1}$$

where

$$H_e^{(0)}=\sum_{j=1}^{N}\left\{-\frac{\hbar^2}{2m}\nabla_j^2-e^2v(\mathbf{r}_j,\underline{R})+\frac{1}{2}e^2\sum_{j'}{}'|\mathbf{r}_j-\mathbf{r}_{j'}|^{-1}\right\}, \tag{2.2}$$

$$H_L=\sum_l\left\{-\frac{\hbar^2}{2M_l}\nabla_l^2+\frac{1}{2}\sum_{l'}{}'W_{ll'}(\mathbf{R}_l-\mathbf{R}_{l'})\right\}. \tag{2.3}$$

In Eqs. (2.1) and (2.2), $H_e^{(0)}$ is the energy of N electrons of the cluster, including their interactions $v(\mathbf{r},\underline{R})$ with nuclei of the cluster and ions of the embedding region whose position vectors $\mathbf{R}_l$ are collectively denoted $\underline{R}$. In Eqs. (2.1) and (2.3), H_L is the energy of the classical point masses, where $W_{ll'}$ includes all pairwise interactions amount cluster nuclei and embedding region ions. It can be generalized to include higher-order (e.g. three-body) interactions.

The interaction $v(\mathbf{r},\underline{R})$ will be of Coulomb type

$$v(\mathbf{r},\underline{R})=\sum_l Q_l|\mathbf{r}-\mathbf{R}_l|^{-1}, \tag{2.4}$$

where Q_l is the charge in units $|e|$ of nucleus or ion l. In this section, atoms will be treated as rigid. In the Appendix, the shell model for ionic crystals will be introduced, in which each ion consists of harmonically coupled charged core and shell. The potential $W_{ll'}$ includes both Coulomb and short-range interactions. The interaction between cluster nuclei and embedding region atoms should include short-range terms, and also Coulomb terms if the embedding atoms are charged ions.

We first apply the adiabatic approximation to the Schrödinger equation for $H^{(0)}(\underline{r},\underline{R})$ in Eq. (2.1):

$$H^{(0)}\Phi^{(0)}=E^{(0)}\Phi^{(0)}, \tag{2.5}$$

where

$$\Phi^{(0)}(\underline{r},\underline{R})=\psi^{(0)}(\underline{r},\underline{R})\cdot\eta(\underline{R}). \tag{2.6}$$

In Eq. (2.6), $\underline{r}$ stands for the collective set of electronic variables $(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. In general, $\mathbf{r}_j$ should include both the electron's position vector and its spin, but since spin does not enter the rest of the formulation, we omit it here. Next we introduce the harmonic approximation for the atomic vibrations:

$$\underline{R}=(\underline{R}_0+\underline{u}), \tag{2.7}$$

where $\underline{u}$ is the set of small (harmonic) displacements of all the nuclei and atoms. In this approximation, the effective Hamiltonian $\overline{H}_L^{(0)}$ for the perfect crystal is found by taking the expectation value of $H^{(0)}$ with respect to the electronic part of the adiabatic state function, Eq. (2.6). Thus:

$$\overline{H}_L^{(0)}=H_L+\langle\psi^{(0)}|H_e^{(0)}|\psi^{(0)}\rangle, \tag{2.8}$$

where the matrix element implies integration over $\underline{r}$, with $\psi^{(0)}$ normalized. This Hamiltonian must be expanded to second order in $\underline{u}$. It involves:

$$\begin{aligned}V^{(0)}(\underline{r},\underline{R})&=\sum_{j=1}^{N}v(\mathbf{r}_{j'}\underline{R})\\&=V^{(0)}(\underline{r},\underline{R}_0)+\underline{V}_1^{(0)}(\underline{r},\underline{R}_0)^T\cdot\underline{u}\\&\quad+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{V}}_2^{(0)}(\underline{r},\underline{R}_0)\cdot\underline{u},\end{aligned} \tag{2.9}$$

where $\underline{u}$ and $\underline{V}_1^{(0)}$ are column matrices whose elements correspond to Cartesian components of all displacement vectors $\mathbf{u}_l$, T indicates the transpose of the matrix, and $\underline{\underline{V}}_2^{(0)}$ is a square matrix in the same basis. Specifically,

$$V_{1,l\beta}^{(0)}=\left[\frac{\partial}{\partial R_{l\beta}}V^{(0)}(\underline{r},\underline{R})\right]_{\underline{R}=\underline{R}_0} \tag{2.10}$$

and

$$V_{2,l\beta,l'\beta'}^{(0)}=\left[\frac{\partial^2}{\partial R_{l\beta}\partial R_{l'\beta'}}V^{(0)}(\underline{r},\underline{R})\right]_{\underline{R}=\underline{R}_0}. \tag{2.11}$$

In Eqs. (2.10) and (2.11), β and β' label Cartesian components. Similarly we expand

$$\begin{aligned}W&=\frac{1}{2}\sum_{ll'}{}'W_{ll'}\\&=W(\underline{R}_0)+\underline{W}_1(\underline{R}_0)^T\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{W}}_2(\underline{R}_0)\cdot\underline{u}.\end{aligned} \tag{2.12}$$

In Eq. (2.6), the electronic part $\psi^{(0)}$ of the state function depends on the atomistic configuration $\underline{R}$. Thus in the harmonic approximation we should consider

$$\begin{aligned}\psi^{(0)}(\underline{r},\underline{R})&=\psi^{(0)}(\underline{r},\underline{R}_0)+\underline{\psi}_1^{(0)}(\underline{r},\underline{R}_0)^T\cdot\underline{u}\\&\quad+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{\psi}}_2^{(0)}(\underline{r},\underline{R}_0)\cdot\underline{u},\end{aligned} \tag{2.13}$$

in analogy to Eqs. (2.9)–(2.11). However, in Eq. (2.13) we require normalization to be maintained. If we write $\psi^{(0)}(\underline{r},\underline{R}_0)=\psi_0^{(0)}$, then the normalization condition becomes:

$$\begin{aligned}1&=\langle\psi^{(0)}|\psi^{(0)}\rangle\\&=\langle\psi_0^{(0)}|\psi_0^{(0)}\rangle+2\langle\psi_0^{(0)}|\underline{\psi}_1^{(0)}\rangle^T\cdot\underline{u}\\&\quad+2\underline{u}^T\cdot\langle\psi_0^{(0)}|\underline{\underline{\psi}}_2^{(0)}\rangle\cdot\underline{u}+\underline{u}^T\cdot\langle\underline{\psi}_1^{(0)T}|\underline{\psi}_1^{(0)}\rangle\cdot\underline{u}.\end{aligned} \tag{2.14}$$

In Eq. (2.14) we have taken ψ to be real. Now $\langle\psi_0^{(0)}|\psi_0^{(0)}\rangle=1$, and, therefore,

$$\langle\psi_0^{(0)}|(2\underline{\psi}_1^{(0)T}\cdot\underline{u}+2\underline{u}^T\cdot\underline{\underline{\psi}}_2^{(0)}\cdot\underline{u})\rangle=-\underline{u}^T\cdot\langle\underline{\psi}_1^{(0)T}|\underline{\psi}_1^{(0)}\rangle\cdot\underline{u}. \tag{2.15}$$

Now combining Eqs. (2.8)–(2.13), the effective perfect crystal Hamiltonian to second order in $\underline{u}$ takes the form

$$\begin{aligned}\overline{H}_L^{(0)}=\{&T_L+W_0+\underline{W}_1^T\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{W}}_2\cdot\underline{u}+\langle\psi_0^{(0)}|H_{e0}^{(0)}|\psi_0^{(0)}\rangle-e^2\langle\psi_0^{(0)}|\underline{V}_1^{(0)T}|\psi_0^{(0)}\rangle\cdot\underline{u}\\&+2\langle\psi_0^{(0)}|H_{e0}^{(0)}|\underline{\psi}_1^{(0)}\rangle^T\cdot\underline{u}+2\underline{u}^T\cdot\langle\psi_0^{(0)}|H_{e0}^{(0)}|\underline{\underline{\psi}}_2^{(0)}\rangle\cdot\underline{u}\\&-\tfrac{1}{2}e^2\underline{u}^T\cdot\langle\psi_0^{(0)}|(4\underline{V}_1^{(0)T}|\underline{\psi}_1^{(0)}\rangle+\underline{\underline{V}}_2^{(0)}|\psi_0^{(0)}\rangle)\cdot\underline{u}+\underline{u}^T\cdot(\underline{\psi}_1^{(0)T}|H_{e0}^{(0)}|\underline{\psi}_1^{(0)}\rangle\cdot\underline{u}\}.\end{aligned} \tag{2.16}$$

Again, we use a subscript 0 to indicate a quantity evaluated with $\underline{R}=\underline{R}_0$. However, the quantities $\underline{V}_1^{(0)}$, $\underline{\underline{V}}_2^{(0)}$, $\underline{W}_1$, and $\underline{\underline{W}}_2$ are also functions only of $\underline{R}_0$, as in Eqs. (2.10) and (2.11). In Eq. (2.16), T_L is the kinetic energy of point masses from Eq. (2.3):

$$T_L=\sum_l\left[-\frac{\hbar^2}{2M_l}\nabla_l^2\right] . \tag{2.17}$$

The state $\psi_0^{(0)}=\psi^{(0)}(\underline{r},\underline{R}_0)$ is determined variationally, in our work, for the static embedded cluster in the perfect crystal equilibrium configuration $\underline{R}_0$. We introduce $E_I^{(0)}$, the total energy of the perfect static crystal including both quantum cluster and embedding region:

$$E_I^{(0)}=\langle\psi_0^{(0)}|H_{e0}^{(0)}|\psi_0^{(0)}\rangle+W_0 , \tag{2.18}$$

where W is defined in Eq. (2.12), and $W_0=W(\underline{R}_0)$. Thus, within the limits of the variational principle,

$$(H_{e0}^{(0)}+W_0)|\psi_0^{(0)}\rangle\approx E_I^{(0)}|\psi_0^{(0)}\rangle . \tag{2.19}$$

Consider the following two terms from Eq. (2.16):

$$\begin{aligned}2\langle\psi_0^{(0)}|H_{e0}^{(0)}|\underline{\psi}_1^{(0)}\rangle^T\cdot\underline{u}+2\underline{u}^T\cdot\langle\psi_0^{(0)}|H_{e0}^{(0)}|\underline{\underline{\psi}}_2^{(0)}\rangle\cdot\underline{u}&\\ =\langle\psi_0^{(0)}|H_{e0}^{(0)}|(2\underline{\psi}_1^{(0)T}\cdot\underline{u}+2\underline{u}^T\cdot\underline{\underline{\psi}}_2^{(0)}\cdot\underline{u})\rangle&\\ =-(E_I^{(0)}-W_0)\underline{u}^T\cdot\langle\underline{\psi}_1^{(0)T}|\underline{\psi}_1^{(0)}\rangle\cdot\underline{u} .&\end{aligned} \tag{2.20}$$

The last line of Eq. (2.20) follows from Eq. (2.19) and the normalization condition, Eq. (2.15).

The condition that determines the perfect crystal equilibrium configuration $\underline{R}_0$ is

$$\left[\frac{\partial\bar{H}_L^{(0)}}{\partial u_{l\beta}}\right]_{\underline{u}=0}=0 . \tag{2.21}$$

By combining Eqs. (2.16) and (2.20), this reduces to:

$$[\underline{W}_1(\underline{R}_0)-e^2\langle\psi_0^{(0)}(\underline{R}_0)|\underline{V}_1^{(0)}(\underline{R}_0)|\psi_0^{(0)}(\underline{R}_0)\rangle]=0 . \tag{2.22}$$

This result embodies the Hellman-Feynman theorem, that the equilibrium configuration is not affected by the dependence of the state function on $\underline{u}$. The remaining terms, quadratic in $\underline{u}$ in Eqs. (2.16) and (2.20), give the force constant matrix $\underline{\underline{K}}^{(0)}$:

$$\begin{aligned}\underline{\underline{K}}^{(0)}=\{\underline{\underline{W}}_2-e^2\langle\psi_0^{(0)}|\underline{\underline{V}}_2^{(0)}|\psi_0^{(0)}\rangle-4e^2\langle\psi_0^{(0)}|\underline{V}_1^{(0)T}|\underline{\psi}_1^{(0)}\rangle&\\ +2\langle\underline{\psi}_1^{(0)T}|(H_{e0}^{(0)}+W_0-E_I^{(0)})|\underline{\psi}_1^{(0)}\rangle\} .&\end{aligned} \tag{2.23}$$

This expression is worth comment. The first term $\underline{\underline{W}}_2$ contains the force constants of classical atoms of the embedding region plus the contribution from Coulomb interactions of the bare nuclei of the cluster. The second term dresses the nuclear Coulomb interaction with electrons in state $\psi_0^{(0)}=\psi^{(0)}(\underline{r},\underline{R}_0)$, and the remaining two terms correct this for the fact that the electrons follow the nuclear and atomic motions as expressed in Eq. (2.13), subject to normalization.

The results obtained so far provide a sensitive test of the method used to analyze the quantum molecular cluster, and of its compatibility with the model used for the embedding region. Having calculated $\psi_0^{(0)}$, Eq. (2.22) for the equilibrium configuration can be used either by setting $\underline{R}_0$ at the experimental value and comparing the calculated value of the left-hand side with zero, or by allowing the cluster to relax to equilibrium and comparing the resultant configuration with the uniform experimental lattice spacing. Beyond this, however, the model can be used to evaluate the phonon dispersion relations of the crystal, using Eq. (2.23) to calculate the normal mode angular frequencies $\omega_j(\mathbf{k})$. The comparison of these results with experiment is a particularly good test of the model. In practice, the curvature of the total energy as a function of atomic displacements in the quantum cluster can be used to determine classical force constants. The elastic properties of the corresponding classical model of the crystal can then be compared with experiment. Once a cluster method has been developed to the point of being reliable at the level of lattice spacing and force constants, Eq. (2.23), its use to derive anharmonic interatomic forces may be undertaken with confidence.

The final form of the effective perfect crystal Hamiltonian is found from Eq. (2.16), using Eqs. (2.18), (2.20), (2.22), and (2.23):

$$\bar{H}_L^{(0)}=E_I^{(0)}+(T_L+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{K}}^{(0)}\cdot\underline{u}) . \tag{2.24}$$

Upon quantizing the vibration variables $\underline{u}$, we will obtain the perfect crystal phonon Hamiltonian. Following the notation of Maradudin, Montroll, and Weiss[8] we rewrite $u_{l\beta}$ as $u_\beta(^l_n)$, which refers to the primitive unit cell l and the basis atom n in the unit cell. We then introduce the transformation

$$u_\beta\begin{bmatrix}l\\n\end{bmatrix}=(N_1M_n)^{-1/2}\sum_{\mathbf{k}j}\varepsilon_{\beta j}^n(\mathbf{k})\exp(2\pi i\mathbf{k}\cdot\mathbf{l})\times\left[\frac{\hbar}{2\omega_j(\mathbf{k})}\right]^{1/2}(a_{-\mathbf{k}j}^{+}+a_{\mathbf{k}j}) . \tag{2.25}$$

In Eq. (2.25), N_1 is the number of unit cells in a large sample of the crystal subject to periodic (Born–von Karman) boundary conditions, $j=1,2,3$ labels phonon branches, $\varepsilon_j^n(\mathbf{k})$ are polarization vectors, $\omega_j(\mathbf{k})$ are normal mode angular frequencies derived from the perfect crystal vibration Hamiltonian $(T_L+\frac{1}{2}\underline{u}^T\cdot\underline{\underline{K}}^{(0)}\cdot\underline{u})$, and $a_{\mathbf{k}j}^{+}$ and $a_{\mathbf{k}j}$ are phonon creation and annihilation operators respectively. Then in Eq. (2.24):

$$(T_L+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{K}}^{(0)}\cdot\underline{u})=\sum_{\mathbf{k}j}\hbar\omega_j(\mathbf{k})(a_{\mathbf{k}j}^{+}a_{\mathbf{k}j}+\tfrac{1}{2}) . \tag{2.26}$$

III. THE DEFECT CRYSTAL

We now introduce the impurity into the molecular cluster. Let Qe and M be its nuclear charge and mass, respectively, $\mathbf{x}$ its nuclear position, and n its number of electrons. The Hamiltonian of the system is

$$H=(H_L+H_e+H_I) . \tag{3.1}$$

In Eq. (3.1), H_L is the kinetic and potential energy of classical atoms and nuclei of the host crystal already introduced in Eq. (2.3), H_e is the energy of the $(N+n)$ electrons of the defect cluster, analogous to Eq. (2.2) for the perfect crystal (which had only N electrons):

$$H_e=\sum_{j=1}^{N+n}\left\{-\frac{\hbar^2}{2m}\nabla_j^2-e^2 v(\mathbf{r}_j,\underline{R})+e^2\sum_{j'}{}'\,|\mathbf{r}_j-\mathbf{r}_{j'}|^{-1}\right\} . \tag{3.2}$$

The remaining term in Eq. (3.1), H_I, contains the kinetic energy of the impurity nucleus, its interaction with the point-mass atoms and nuclei of the host crystal, and with all the electrons of the quantum cluster. Specifically,

$$H_I=\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+Qe^2 v(\mathbf{x},\underline{R})-Qe^2\sum_{j=1}^{N+n}|\mathbf{r}_j-\mathbf{x}|^{-2}\right\} . \tag{3.3}$$

For a light impurity, its position variable **x** will not be limited to harmonic oscillation, in contrast to the other nuclei and point-mass atoms of the system, Eq. (2.7).

We shall obtain the effective Hamiltonian for the atoms and nuclei of the system. The impurity nucleus will react only to the average electronic distribution, as will the atoms and other nuclei. This is justified for muonium, where $(M/m)=207$, and for hydrogen, where $(M/m)=1836$, for example. The effective Hamiltonian will be given in two forms. In the first perfect crystal phonons will be featured. This will lead to analytical expressions for linear and quadratic impurity-phonon coupling coefficients. In the second form, the normal modes of the defect crystal will be featured. This will lead to expressions for the distortion field of the defect, and to the perturbed phonon dispersion relation due to the defect.

We again adopt the adiabatic approximation, now in the form:

$$\Phi(\underline{r},\mathbf{x},\underline{R})=\psi(\underline{r},\mathbf{x},\underline{R})\xi(\mathbf{x})\eta(\underline{r}) , \tag{3.4}$$

an extension of Eq. (2.6) to include the impurity. This assumes that the electrons follow the impurity adiabatically. In this work, we consider an interstitial impurity. If it is substitutional, a trivial modification needs to be introduced in the formalism. Now the collective set of electron coordinates is $\underline{r}=\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N+n}$. The effective Hamiltonian for the defect crystal including the impurity is

$$\begin{aligned}\overline{H}_L=&\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+Qe^2 v(\mathbf{x},\underline{R})\right.\\&\left.-Qe^2\left\langle\psi\left|\sum_{j=1}^{N+n}|\mathbf{r}_j-\mathbf{x}|^{-1}\right|\psi\right\rangle\right\}\\&+(H_L+\langle\psi^{(0)}|H_e^{(0)}|\psi^{(0)}\rangle)\\&+(\langle\psi|H_e|\psi\rangle-\langle\psi^{(0)}|H_e^{(0)}|\psi^{(0)}\rangle) .\end{aligned} \tag{3.5}$$

In Eq. (3.5) we have written $\overline{H}_L$ as the sum of three terms: the impurity nucleus term, involving **x**, the perfect crystal term including electronic part as given in Eq. (2.2), and a term that corrects the electronic part from perfect crystal to defect crystal. H_e is given in Eq. (3.2) and differs from $H_e^{(0)}$ only in the number of electrons involved in the cluster.

As in Sec. II, Eq. (2.7), we expand $\overline{H}_L$ to second order in small host-crystal atom displacements from perfect crystal equilibrium $\underline{R}_0$, as determined from Eqs. (2.21) and (2.22). The second term in Eq. (3.5), referring to the perfect crystal, gives $\overline{H}_L^{(0)}$ Eqs. (2.8) and (2.24). The remaining terms, apart from impurity kinetic energy, are

$$\begin{aligned}&Qe^2\{V(\mathbf{x},\underline{R}_0)+\underline{V}_1(\mathbf{x},\underline{R}_0)^T\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{V}}_2(\mathbf{x},\underline{R}_0)\cdot\underline{u}\} ,\\&-Qe^2\{\langle\psi_0|V(\underline{r},\mathbf{x})|\psi_0\rangle+2\langle\psi_0|V(\underline{r},\mathbf{x})|\underline{\psi}_1^T\rangle\cdot\underline{u}\\&\qquad+2\underline{u}^T\cdot\langle\psi_0|V(\underline{r},\mathbf{x})|\underline{\underline{\psi}}_2\rangle\cdot\underline{u}+\underline{u}^T\cdot\langle\underline{\psi}_1|V(\underline{r},\mathbf{x})|\underline{\psi}_1^T\rangle\cdot\underline{u}\}\\&\qquad+\{F_d(\underline{u})-F_p(\underline{u})\} .\end{aligned} \tag{3.6}$$

The notation $V(\underline{r},\mathbf{x})$ means

$$\sum_{j=1}^{N+n}|\mathbf{r}_j-\mathbf{x}|^{-1} .$$

In Eq. (3.6), the quantities F_d and F_p refer to the defect and perfect crystals, respectively. F_p consists of all the terms in Eq. (2.16) that involve the perfect crystal cluster electronic state function $\psi^{(0)}$. F_d is identical to F_p in form, but it involves the defect crystal state function ψ, Eq. (3.4), and operators H_e, Eq. (3.2), and

$$V(\underline{r},\underline{R})=\sum_{j=1}^{N+n}v(\mathbf{r}_j,\underline{R}) , \tag{3.7}$$

where v is given in Eq. (2.4). The normalization condition for $\psi^{(0)}$, Eq. (2.14), applies also to ψ. Just as $|\psi_0^{(0)}\rangle$ approximately satisfies Eq. (2.19), so $|\psi_0\rangle$ approximately satisfies the eigenvalue equation:

$$\{H_{e0}-Qe^2V(\underline{r},\mathbf{x})+Qe^2V(\mathbf{x},\underline{R}_0)+W_0\}|\psi_0\rangle=E_I(\mathbf{x})|\psi_0\rangle , \tag{3.8}$$

where $E_I(\mathbf{x})$ is the total energy of the crystal containing the impurity with its nucleus at **x**, undistorted from the perfect crystal configuration $\underline{R}_0$. Normalization and the eigenvalue Eqs. (2.19) and (3.8) combine in a similar manner as in the perfect crystal case. The final result for $\overline{H}_L$, Eq. (3.5), when Eq. (3.6) is simplified, has the following form:

$$\begin{aligned}\overline{H}_L=&-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+[E_I(\mathbf{x})-E_I^{(0)}]+\overline{H}_L^{(0)}\\&+\underline{G}(\mathbf{x})^T\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot[(\underline{\underline{K}}(\mathbf{x})-\underline{\underline{K}}^{(0)})+\underline{\underline{B}}(\mathbf{x})]\cdot\underline{u} ,\end{aligned} \tag{3.9}$$

where $\overline{H}_L^{(0)}$ is given in Eq. (2.24), and where $\underline{\underline{K}}(\mathbf{x})$ has a form identical to $\underline{\underline{K}}^{(0)}$, Eq. (2.23), except that all superscripts (0) are removed. Thus,

$$\begin{aligned}\overline{H}_L=&\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+E_I(\mathbf{x})\right\}\\&+\left\{\sum_l\left[-\frac{\hbar^2}{2M_l}\nabla_l^2\right]+\frac{1}{2}\underline{u}^T\cdot\underline{\underline{K}}^{(0)}\cdot\underline{u}\right\}\\&+\underline{G}(\mathbf{x})^T\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot[(\underline{\underline{K}}(\mathbf{x})-\underline{\underline{K}}^{(0)})+\underline{\underline{B}}(\mathbf{x})]\cdot\underline{u} .\end{aligned} \tag{3.10}$$

In Eqs. (3.9) and (3.10) the linear and quadratic impurity-host vibration coefficients $\underline{G}(\mathbf{x})$ and $\underline{\underline{B}}(\mathbf{x})$ are

$$\underline{G}(\mathbf{x})=\{Qe^2\underline{V}_1(\mathbf{x},\underline{R}_0) \\ -e^2[\langle\psi_0|\underline{V}_1|\psi_0\rangle-\langle\psi_0^{(0)}|\underline{V}_1^{(0)}|\psi_0^{(0)}\rangle]\} \,, \quad (3.11)$$

$$\underline{\underline{B}}(\mathbf{x})=2Qe^2[\langle\underline{\psi}_1|V(\mathbf{x},\underline{R}_0)-V(\underline{r},\mathbf{x})|\underline{\psi}_1^T\rangle] \,. \quad (3.12)$$

We note that in Eqs. (3.9) and (3.10) $\underline{\underline{K}}$ is a function of $\mathbf{x}$, because it has $E_I^{(0)}$ of Eq. (2.23) replaced by $E_I(\mathbf{x})$. This expresses the fact that the normal mode spectrum of the defect crystal depends on the impurity's position.

The expressions obtained in Eqs. (3.10)–(3.12) have relatively simple physical interpretations and are in a practical form for numerical evaluation. In Eq. (3.10) the first term is an impurity Hamiltonian, with effective potential $E_I(\mathbf{x})$, the energy of the undistorted crystal as a function of impurity position. Given a solution for the electronic state ψ_0 from Eq. (3.8) with impurity position $\mathbf{x}$ fixed, the impurity state function $\zeta(\mathbf{x})$ may be solved for zeroth order from the effective Hamiltonian:

$$\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+E_I(\mathbf{x})\right\} .$$

As discussed below, this may, in principle, be augmented by the zero-point energy of the perturbed-phonon field, Eq. (3.20). In Fig. 1 of Ref. 6, $E_I(\mathbf{x})$ is illustrated for the case of muonium in NaF. Also in that reference, two methods are described for estimating $\zeta(\mathbf{x})$. The second term in Eq. (3.10) is the perfect lattice Hamiltonian. In the third term, the linear coupling coefficient $G_{l\beta}(\mathbf{x})$ is the force on the impurity due to atom or nucleus l. It has two parts, from Eq. (3.11). From Eqs. (2.4) and (2.9)

$$Qe^2V_{1,l\beta}(\mathbf{x},\underline{R}_0)=QQ_le^2\left[\frac{\partial}{\partial R_{l\beta}}|\mathbf{x}-\mathbf{R}_l|^{-1}\right]_{\mathbf{R}_l=\mathbf{R}_{l0}} . \quad (3.13)$$

This is the negative of the force on the nucleus or atom at $\mathbf{R}_l$ due to the impurity nucleus Q at $\mathbf{x}$. The other term in Eq. (3.11) has as its $l\beta$ element:

$$-e^2\left\{\int d\tau_{N+n}|\psi(\underline{r},\mathbf{x},\underline{R}_0)|^2Q_l\left[\frac{\partial}{\partial R_{l\beta}}\left[\sum_{j=1}^{N+n}|\mathbf{r}_j-\mathbf{R}_l|^{-1}\right]\right]_{\mathbf{R}_l=\mathbf{R}_{l0}} \\ -\int d\tau_N|\psi^{(0)}(\underline{r},\underline{R}_0)|^2Q_l\left[\frac{\partial}{\partial R_{l\beta}}\left[\sum_{j=1}^{N}|\mathbf{r}_j-\mathbf{R}_l|^{-1}\right]\right]_{\mathbf{R}_l=\mathbf{R}_{l0}}\right\} . \quad (3.14)$$

In Eq. (3.14), the two terms represent a simple Coulomb effect, giving the negative of the force on nucleus or atom l of the host crystal undistorted, due to the difference in electronic charge densities $-e|\psi_0|^2$ and $-e|\psi_0^{(0)}|^2$ when the impurity is present and when it is absent. When it is absent, the crystal is in equilibrium in configuration $\underline{R}_0$. In practice, $\underline{G}(x)$ can be evaluated simply from the gradient of the total energy with respect to atomic displacements. Nevertheless, the integrals in Eq. (3.14) can be evaluated numerically. In Ref. 6, the former method was applied, to muonium in NaF, with $\mathbf{x}$ fixed at the interstitial site, and the deformation potential parameter was estimated. In Eq. (3.10) there are two contributions to the quadratic impurity-host coupling. One, $[\underline{\underline{K}}(\mathbf{x})-\underline{\underline{K}}^{(0)}]$ is the change of the force constants due to the introduction of n electrons with the impurity, and the other, $\underline{\underline{B}}(\mathbf{x})$, Eq. (3.12), is due to the interaction of the impurity nucleus of charge Q with its surroundings, mediated by the electronic state function's gradient with respect to host atom or nuclear positions:

$$\psi_{1,l\beta}(\underline{r},\mathbf{x},\underline{R}_0)=\left[\frac{\partial}{\partial R_{l\beta}}\psi(\underline{r},\mathbf{x},\underline{R}_0)\right]_{\underline{R}=\underline{R}_0} . \quad (3.15)$$

The impurity-phonon Hamiltonian $\overline{H}_L$ of Eq. (3.10) can be reexpressed in terms of the normal modes of the defect crystal, in which the impurity coordinate $\mathbf{x}$ is still kept separate from those of the host crystal $\underline{u}$. The well-known procedure is to introduce new host variables:

$$\underline{u}'(\mathbf{x})=[\underline{u}+\underline{d}(\mathbf{x})] \,, \quad (3.16)$$

which are still harmonic variables, but now oscillate about displaced equilibrium positions $[\underline{R}_0+\underline{d}(\mathbf{x})]$, where $\underline{d}(\mathbf{x})$ represents the distortion of the crystal by the impurity at $\mathbf{x}$. To satisfy the equilibrium condition we choose $\underline{d}$ so that the effective Hamiltonian $\overline{H}_L$ has no linear terms in $\underline{u}'$:

$$\underline{d}(\mathbf{x})=-[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]^{-1}\cdot\underline{G}(\mathbf{x}) \,. \quad (3.17)$$

In practice, this distortion field is determined by minimizing the total energy of the crystal self-consistently with respect to $\underline{d}(\mathbf{x})$ and $\psi(\underline{r},\mathbf{x},\underline{R})$ in static lattice approximation. In Ref. 6, the nearest-neighbor displacements due to muonium at the interstitial site in NaF were found to be negligible. This would not be the case, however, if $\mathbf{x}$ were fixed at the center of a face of the basic cube of the crystal lattice. Then from Eqs. (3.10), (3.16), and (3.17),

$$\overline{H}_L=\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+[E_I(\mathbf{x};\underline{R}_0+\underline{d})]\right\} , \\ +\left\{\sum_l\left[-\frac{\hbar^2}{2M_l}\nabla_l^2\right]+\frac{1}{2}\underline{u}^T\cdot[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]\cdot\underline{u}'\right\} . \quad (3.18)$$

In Eq. (3.18), the effective potential seen by the impurity when the crystal is distorted to configuration $[\underline{R}_0+\underline{d}(\mathbf{x})]$ is

$$E_I(\mathbf{x},\underline{R}_0+\underline{d})=\{E_I(\mathbf{x};\underline{R}_0) -\tfrac{1}{2}\underline{G}(\mathbf{x})^T\cdot[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]^{-1}\cdot\underline{G}(\mathbf{x})\} \ . \tag{3.19}$$

Now, in Eq. (3.18), the normal-mode frequencies of the crystal $\omega'_{kj}(\mathbf{x})$, determined by the effective force constants $[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]$, depend on the impurity position $\mathbf{x}$. This will apply mainly to the localized modes of the defect, with the long-wave modes little affected. In general, however, even at absolute zero, the phonon field's zero-point energy will contribute to the effective potential for the impurity. This contribution is

$$\sum_{kj}\tfrac{1}{2}\hbar\omega'_{kj}(\mathbf{x}) \ . \tag{3.20}$$

In Ref. 2, an example is given of estimating ω' for the principal localized mode associated with a Cu^+ impurity in NaF.

IV. SUMMARY

We have considered a crystal, which is simulated by a quantum molecular cluster of atoms embedded in a classical crystal. We have derived expressions that show explicitly, in terms of the state function, how the electronic structure of the cluster contributes to computed physical features of such a crystal.

For the perfect crystal, the role of the electrons in dressing the nuclear contribution to the force constants is shown in Eq. (2.23). The perfect crystal equilibrium condition, Eq. (2.22) provides a test of the method used for electronic structure analysis, and of its compatibility with the classical model of the embedding region.

When an impurity is introduced into the crystal at position $\mathbf{x}$, consisting of a nucleus and n electrons, the effective potential which its nucleus sees, $E_I(\mathbf{x})$, Eqs. (3.8) and (3.10), depends on the self-consistent field of all the electrons: its own and those of the cluster. This effective potential can be used to determine the state function of the impurity nucleus. The linear coefficient of impurity-phonon interaction $\underline{G}(\mathbf{x})$, Eq. (3.11), includes the Coulomb forces on surrounding atoms of the impurity nucleus, Eq. (3.13), and of the modification Eq. (3.14), of electronic charge density from its perfect crystal equilibrium state $\psi_0^{(0)}$ to its impurity state ψ_0. For the quadratic coefficient of impurity-phonon interaction, there are two contributions, Eq. (3.10). One, $[\underline{\underline{K}}(\mathbf{x})-\underline{\underline{K}}^{(0)}]$, is due to the change of electronic state (including the increase of number by n). The other, $\underline{\underline{B}}(\mathbf{x})$, is the impurity nuclear contribution, mediated by the gradient of the cluster state function with respect to atomic positions. The crystal distortion $\underline{d}(\mathbf{x})$, Eq. (3.17), and its associated energy, Eq. (3.19), emerge naturally from the transformation to defect crystal phonons, Eq. (3.16).

In static crystal embedded cluster calculations,[1] we evaluate the impurity potentials, $E_I(\mathbf{x},\underline{R}_0)$ for the undistorted defect crystal and $E_I(\mathbf{x},\underline{R}_0+\underline{d})$ for the relaxed crystal Eqs. (3.8) and (3.19). We also evaluate the cluster electronic densities $|\psi(\underline{r},\mathbf{x},\underline{R}_0)|^2$ and $|\psi^{(0)}(\underline{r},\underline{R}_0)|^2$ for undistorted defect and perfect crystals, respectively, that are needed to evaluate the linear impurity-phonon coefficient $\underline{G}(\mathbf{x})$, Eqs. (3.11) and (3.14). However, an easier procedure is to evaluate the energy gradient with respect to atomic displacements from perfect crystal sites. The quadratic coefficient, Eqs. (3.10), (2.23), and (3.12), involve the gradients of the cluster state function with respect to atomic positions $\underline{\psi}_1$, Eq. (2.13). These can be evaluated explicitly from embedded cluster calculations also, although we have not done it yet.

From the above it is clear that practical methods exist, which have been applied,[6] to numerically implement the analytical processes described in this work. When it comes to determining the light impurity wave function $\zeta(\mathbf{x})$, Eq. (3.4), from the effective potentials $E_I(\mathbf{x},\underline{R}_0)$ or $E_I(\mathbf{x},\underline{R}_0+\underline{d})$, Eqs. (3.8) and (3.19), one may consider an analytical fit as a function of $\mathbf{x}$, with or without the tight-binding approximation.

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APPENDIX

1. The shell model

For ionic crystals, the shell model[7] has been found to correlate bulk harmonic and static properties quite well. These properties include equilibrium lattice spacing, high- and low-frequency dielectric constants, elastic constants, and phonon dispersion relations. The shell model is therefore suitable for simulating the embedding region for the cluster method described in Secs. I and II.

In the shell model, each ion may be described by two point charges, referred to as a shell of charge $Y_l|e|$ and a core of charge $(Q_l-Y_l)|e|$, where $Q_l|e|$ is the total ionic charge of ion l. The core and shell of a given ion are assumed to be harmonically coupled, with force constant K_l. In addition to Coulomb forces, short-range forces are assumed to act between shells of pairs of ions. To describe harmonic bulk properties, these short-range forces may be taken to be harmonic also. However, for defect simulation it has been found to be effective to use anharmonic forms.[9] The Coulomb force between the core and the shell of a given ion is omitted.

In order to extend our formulation to the case of a shell-model embedding region, we introduce, in place of ionic charge Q_l, Eq. (2.4), two charges, Q_{lc} and Q_{ls}, respectively, for core and shell:

$$Q_{lc}=(Q_l-Y_l),\quad Q_{ls}=Y_l \ . \tag{A1}$$

Similarly there are now two sets of ionic coordinates $\underline{R}=(\underline{R}_c,\underline{R}_s)$. For the harmonic approximation, Eq. (2.7), we introduce displacements $\underline{u}_c$ and $\underline{u}_s$, and write

$$\underline{u}=(\underline{u}_c,\underline{u}_s) \ , \tag{A2}$$

a column vector whose first set of elements is $\underline{u}_c$, followed by $\underline{u}_s$. The harmonic expansion coefficients are similarly generalized. For example, Eq. (2.10) is replaced by

$$V^{(0)}_{1,l\tau\beta}=\left[\frac{\partial}{\partial R_{l\tau\beta}}V^{(0)}(\underline{r},\underline{R})\right]_{\underline{R}=\underline{R}_0}, \quad \tau=c,s \ . \tag{A3}$$

Similar generalizations apply to Eqs. (2.11) to (2.13).

2. The perfect crystal

We write the effective perfect crystal Hamiltonian to second order. From Eq. (2.16), with Eqs. (2.19) and (2.20), we have

$$\overline{H}_L^{(0)}=E_I^{(0)}+T_L+\underline{G}^{(0)T}\cdot\underline{u}+\tfrac{1}{2}\underline{u}^T\cdot\underline{\underline{K}}^{(0)}\cdot\underline{u} \ , \tag{A4}$$

where

$$\underline{G}^{(0)}=(\underline{W}_1-e^2\langle\psi^{(0)}|\underline{V}_1^{(0)}|\psi^{(0)}\rangle) \ , \tag{A5}$$

as in Eq. (2.22), and $\underline{\underline{K}}^{(0)}$ is given in Eq. (2.23). We now write

$$T_L=\tfrac{1}{2}(\underline{p}_c^T\cdot\underline{\underline{M}}_c^{-1}\cdot\underline{p}_c+\underline{p}_s^T\cdot\underline{\underline{M}}_s^{-1}\cdot\underline{p}_s) \ . \tag{A6}$$

In Eq. (A6) we have attributed masses M_{lc} and M_{ls} to cores and shells, respectively. Conventionally, the shell masses are taken to be zero, and we shall introduce this feature later. Since the shell model is classical, we have used the canonical Hamiltonian formulation, in terms of momenta $\mathbf{p}_{lc}$ and $\mathbf{p}_{ls}$, collectively denoted $\underline{p}=(\underline{p}_c,\underline{p}_s)$, and have introduced the diagonal inverse mass matrix $\underline{\underline{M}}^{-1}$, expressed in terms of submatrices $\underline{\underline{M}}_c^{-1}$ and $\underline{\underline{M}}_s^{-1}$. Now with the shell model, $\underline{G}^{(0)}$ decomposes into core and shell parts, as in Eq. (A2), and $\underline{\underline{K}}^{(0)}$ decomposes into submatrices $\underline{\underline{K}}^{(0)}_{\tau\tau'}$, where both τ and τ' can take values c or s. Thus,

$$\begin{aligned}\overline{H}_L^{(0)}=E_I^{(0)}&+\tfrac{1}{2}(\underline{p}_c^T\cdot\underline{\underline{M}}_c^{-1}\cdot\underline{p}_c+\underline{p}_s^T\cdot\underline{\underline{M}}_s^{-1}\cdot\underline{p}_s)\\&+(\underline{G}_c^{(0)T}\cdot\underline{u}_c+\underline{G}_s^{(0)T}\cdot\underline{u}_s)\\&+\tfrac{1}{2}(\underline{u}_c^T\cdot\underline{\underline{K}}_{cc}^{(0)}\cdot\underline{u}_c+\underline{u}_s^T\cdot\underline{\underline{K}}_{sc}^{(0)}\cdot\underline{u}_c\\&+\underline{u}_c^T\cdot\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{u}_s+\underline{u}_s^T\cdot\underline{\underline{K}}_{ss}^{(0)}\cdot\underline{u}_s) \ .\end{aligned} \tag{A7}$$

Physically, each ion only has one vector degree of freedom, say $\mathbf{u}_{lc}$. The shell variables $\underline{u}_s$ are merely an empirical representation of the polarizability of the electronic cloud around the ions. We must therefore eliminate $\underline{u}_s$ from the formalism. We do this by solving the canonical Hamiltonian equations of motion:

$$\dot{p}_{l\tau\beta}=-\frac{\partial}{\partial u_{l\tau\beta}}\overline{H}_L^{(0)}, \quad \dot{u}_{l\tau\beta}=\frac{\partial}{\partial p_{l\tau\beta}}\overline{H}_L^{(0)} \ , \tag{A8}$$

where $\tau=c$ or s, and the dot stands for time derivative. For $\underline{u}_s$ we obtain

$$\underline{\underline{M}}_s\cdot\ddot{\underline{u}}_s=-(\underline{G}_s^{(0)}+\underline{\underline{K}}_{sc}^{(0)}\cdot\underline{u}_c+\underline{\underline{K}}_{ss}^{(0)}\cdot\underline{u}_s) \ . \tag{A9}$$

If we now set $\underline{\underline{M}}_s=0$, so that all the mass of an ion is associated with its core, then, since the left-hand side of Eq. (A9) is zero, the right-hand side gives

$$\underline{u}_s=-\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot(\underline{G}_s^{(0)}+\underline{\underline{K}}_{sc}^{(0)}\cdot\underline{u}_c) \ . \tag{A10}$$

For shells of zero mass, their kinetic energy in Eq. (A7) becomes zero. When we substitute for $\underline{u}_s$ from Eq. (A10) into $\overline{H}_L^{(0)}$, Eq. (A7), and simplify, we obtain

$$\begin{aligned}\overline{H}_L^{(0)}=&(E_I^{(0)}-\tfrac{1}{2}\underline{G}_s^{(0)T}\cdot\underline{\underline{K}}_{ss}^{(0)-1}\cdot\underline{G}_s^{(0)})\\&+\{\tfrac{1}{2}\underline{p}_c^T\cdot\underline{\underline{M}}_{cc}^{-1}\cdot\underline{p}_c\\&\quad+\tfrac{1}{2}\underline{u}_c^T\cdot(\underline{\underline{K}}_{cc}^{(0)}-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)-1}\cdot\underline{\underline{K}}_{sc}^{(0)})\cdot\underline{u}_c\}\\&+(\underline{G}_c^{(0)T}-\underline{G}_s^{(0)T}\cdot\underline{\underline{K}}_{ss}^{(0)-1}\cdot\underline{\underline{K}}_{sc}^{(0)})\cdot\underline{u}_c \ .\end{aligned} \tag{A11}$$

From Eq. (A11) we see the following features arising from the effects of the shells on the core dynamics. First, the equilibrium crystal energy $E_I^{(0)}$, Eq. (2.24), is modified by the shell self-energy term

$$-\tfrac{1}{2}\underline{G}_s^{(0)T}\cdot\underline{\underline{K}}_{ss}^{(0)-1}\cdot\underline{G}_s^{(0)} \ .$$

Second, the crystal equilibrium condition, Eq. (2.22), which is $\underline{G}^{(0)}=0$ from the definition of Eq. (A5), is modified to

$$\underline{G}_c^{(0)}-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{G}_s^{(0)}=0 \ . \tag{A12}$$

Third, the force constant matrix $\underline{\underline{K}}^{(0)}$, Eq. (2.23), is modified to

$$\underline{\underline{K}}_{cc}^{(0)}-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{\underline{K}}_{sc}^{(0)} \ . \tag{A13}$$

The difference between $\underline{G}^{(0)}$, Eq. (A5), and $\underline{G}_c^{(0)}$, Eq. (A12), is that in the latter Q_l is replaced by $Q_{lc}=(Q_l-Y_l)$, and similarly for $\underline{\underline{K}}^{(0)}$, Eq. (2.23) and $\underline{\underline{K}}_{cc}^{(0)}$, Eq. (A13). When the equilibrium condition, Eq. (A12), is applied, we obtain the effective crystal Hamiltonian for the shell model, replacing Eq. (2.24):

$$\begin{aligned}\overline{H}_L^{(0)}=&(E_I^{(0)}-\tfrac{1}{2}\underline{G}_s^{(0)T}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{G}_s^{(0)})\\&+\{\tfrac{1}{2}\underline{p}_c^T\cdot\underline{\underline{M}}_{cc}^{-1}\cdot\underline{p}_c\\&\quad+\tfrac{1}{2}\underline{u}_c^T\cdot(\underline{\underline{K}}_{cc}^{(0)}-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{\underline{K}}_{sc}^{(0)})\cdot\underline{u}_c\} \ .\end{aligned} \tag{A14}$$

3. The defect crystal

Consider the effective Hamiltonian $\overline{H}_L$ for light impurity-crystal interaction, Eq. (3.10). We rewrite $\overline{H}_L$ to include the term $\underline{G}^{(0)T}\cdot\underline{u}$ from Eq. (A4), which comes from expanding $\overline{H}_L$ in powers of $\underline{u}$ in Eq. (3.5), before applying the perfect crystal equilibrium condition, Eq. (2.21) in (A11). Then, using Eq. (2.17), Eq. (3.10) becomes

$$\begin{aligned}\overline{H}_L=&\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+E_I(\mathbf{x})\right\}+T_L\\&+\tfrac{1}{2}\underline{u}^T\cdot[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]\cdot\underline{u}+[\underline{G}^{(0)}+\underline{G}(\mathbf{x})]^T\cdot\underline{u} \ .\end{aligned} \tag{A15}$$

The perfect crystal derivation of $\overline{H}_L^{(0)}$ for the shell model, leading from Eq. (A4) to Eq. (A11), can now be followed, with $[\underline{G}^{(0)}+\underline{G}(\mathbf{x})]$ replacing $\underline{G}^{(0)}$, and with $[\underline{\underline{K}}(\mathbf{x})+\underline{\underline{B}}(\mathbf{x})]$ replacing $\underline{\underline{K}}^{(0)}$. We then introduce the perfect crystal equilibrium condition by using Eq. (A12) to substitute for $[\underline{G}_c^{(0)T}\cdot\underline{u}_c]$. We also introduce the perfect crystal force constant matrix, Eq. (A13), by adding and subtracting the quadratic terms in $\underline{u}_c$ of Eq. (A11). The resulting expression for $\overline{H}_L$ has the form

$$\bar{H}_L=\left\{-\frac{\hbar^2}{2M}\nabla_{\mathbf{x}}^2+E_I(\mathbf{x})+E_I^{(s)}(\mathbf{x})\right\}+\{\tfrac{1}{2}\underline{p}_c{}^T\cdot\underline{\underline{M}}_{cc}^{-1}\cdot\underline{p}_c+\tfrac{1}{2}\underline{u}_c{}^T\cdot(\underline{\underline{K}}_{cc}^{(0)}-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{\underline{K}}_{sc}^{(0)})\cdot\underline{u}_c\}$$
$$+[\underline{G}_c(\mathbf{x})-\underline{G}_c^{(s)}(\mathbf{x})]\cdot\underline{u}_c+\tfrac{1}{2}\underline{u}_c{}^T\cdot[\underline{\underline{K}}_{cc}(\mathbf{x})-\underline{\underline{K}}_{cc}^{(0)}+\underline{\underline{B}}_{cc}(\mathbf{x})-\underline{\underline{B}}_{cc}^{(s)}(\mathbf{x})]\cdot\underline{u}_c\ . \tag{A16}$$

In Eq. (A16), the first term is the light impurity part, as in Eq. (3.10), but with an added shell self-energy term $E_I^{(s)}(\mathbf{x})$ analogous to that in Eq. (A11), where

$$E_I^{(s)}(\mathbf{x})=\tfrac{1}{2}[\underline{G}_s^{(0)}+\underline{G}_s(\mathbf{x})]^T\cdot[\underline{\underline{K}}_{ss}(\mathbf{x})+\underline{\underline{B}}_{ss}(\mathbf{x})]^{-1}\cdot[\underline{G}_s^{(0)}+\underline{G}_s(\mathbf{x})]\ . \tag{A17}$$

The second term of Eq. (A16) is the perfect crystal Hamiltonian, precisely as in Eq. (A11), where in T_L, Eq. (A15), we have set the shell kinetic energy to zero. The third term of Eq. (A16) is the linear light impurity-crystal core interaction, where the shell contribution $\underline{G}_c^{(s)}(\mathbf{x})$ to the coupling coefficient is

$$\underline{G}_c^{(s)}(\mathbf{x})=\{[\underline{G}_s^{(0)}+\underline{G}_s(\mathbf{x})]^T\cdot[\underline{\underline{K}}_{ss}(\mathbf{x})+\underline{\underline{B}}_{ss}(\mathbf{x})]^{-1}\cdot[\underline{\underline{K}}_{sc}(\mathbf{x})+\underline{\underline{B}}_{sc}(\mathbf{x})]-\underline{G}_s^{(0)T}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{\underline{K}}_{sc}^{(0)}\}\ . \tag{A18}$$

The fourth and final term of Eq. (A16) is the quadratic impurity-crystal core interaction, where the shell contribution $\underline{\underline{B}}_{cc}^{(s)}(\mathbf{x})$ to the coupling coefficient is

$$\underline{\underline{B}}_{cc}^{(s)}(\mathbf{x})=\{[\underline{\underline{K}}_{cs}(\mathbf{x})+\underline{\underline{B}}_{cs}(\mathbf{x})]\cdot[\underline{\underline{K}}_{ss}(\mathbf{x})+\underline{\underline{B}}_{ss}(\mathbf{x})]^{-1}\cdot[\underline{\underline{K}}_{sc}(\mathbf{x})+\underline{\underline{B}}_{sc}(\mathbf{x})]-\underline{\underline{K}}_{cs}^{(0)}\cdot\underline{\underline{K}}_{ss}^{(0)^{-1}}\cdot\underline{\underline{K}}_{sc}^{(0)}\}\ . \tag{A19}$$

Equations (A16)–(A19) could now be used to derive expressions analogous to Eqs. (3.17) and (3.19) for the distortion field $\underline{d}(\mathbf{x})$ and the distortion energy, including the effect of shells. We shall not do this. We remark, however, that our usual method of static lattice defect simulation[1] is based on the shell model, and that it therefore evaluates the total static potential $[E_I(\mathbf{x})+E_I^{(s)}(\mathbf{x})]$ seen by the impurity, including the shell contribution. Likewise with respect to the distortion field and the associated total static potential for the impurity, the method includes the shell effects.

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