Covalent Bonding in Diamond

K. H. Bennemann

Department of Physics, University of Illinois, Urbana, Illinois

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It is demonstrated that for diamond an extension of the pseudopotential theory using t matrices yields covalent bonding. The covalent bonds arise from multiple scattering of the valence electrons by the lattice ions. It is estimated that about 1.2 valence electrons are localized per bond. We obtain approximately -0.45 rydberg for the cohesive energy. The experimental value for the cohesive energy of diamond is -0.54 rydberg. An approximate expression for the self-consistent crystal field is given in terms of multipole fields. The determination of lattice force constants, fundamental in lattice dynamics, is discussed.

I. THEORY

THE pseudo-crystal-potential theory as developed by Kleinman and Phillips[1] and Cohen, Heine, *et al.*[2] has been used with great success for self-consistent determination of the valence-electron density in metals and semiconductors. It has been shown[3] that an extension of the pseudopotential theory using t matrices yields covalent bonding in diamond. The covalent bonding arises from multiple scattering of the valence electrons by the lattice ions.

The system of valence electrons is described by the Hamilton operator H. The one-electron Green's function $G(\mathbf{r},\mathbf{r}';k_0)$ defined by

$$(H-k_0)G(\mathbf{r},\mathbf{r}';k_0)=\delta(\mathbf{r}-\mathbf{r}') \tag{I.1}$$

can be split in accordance to the procedure in the orthogonalized-plane-wave method as

$$G(\mathbf{r},\mathbf{r}';k_0)=G'(\mathbf{r},\mathbf{r}';k_0)+G''(\mathbf{r},\mathbf{r}';k_0), \tag{I.2}$$

with

$$(H+V_R-k_0)G'(\mathbf{r},\mathbf{r}';k_0)=\delta(\mathbf{r}-\mathbf{r}'), \tag{I.3}$$

and

$$G''(\mathbf{r},\mathbf{r}';k_0)=\frac{1}{\Omega}\sum_{p,p',t}\{\sum_{t'}\varphi_t(\mathbf{r})\varphi_{t'}*(\mathbf{r}')b_t(\mathbf{p})b_{t'}*(\mathbf{p}')$$
$$-\varphi_t*(\mathbf{r}')e^{i\mathbf{p}\cdot\mathbf{r}}-\varphi_t(\mathbf{r})e^{i\mathbf{p}'\cdot\mathbf{r}'}b_t(\mathbf{p})\}G'(\mathbf{p},\mathbf{p}';k_0), \tag{I.4}$$

$$b_t(\mathbf{p})\equiv\langle\varphi_t|\mathbf{p}\rangle. \tag{I.5}$$

V_R is the repulsive potential resulting from orthogonalizing the valence-electron states to the states φ_t of the closed-shell core electrons. $G'(\mathbf{p},\mathbf{p}';k_0)$ is the Fourier transform of $G'(\mathbf{r},\mathbf{r}';k_0)$. In general G'' is much

smaller than G'. Furthermore it becomes obvious that G'' is not much affected by multiple scattering. Writing

$$H+V_R\equiv H_0+\Delta H, \tag{I.6}$$

$$H_0\equiv-\frac{\hbar^2}{2m}\nabla^2+\frac{1}{\Omega}\int d^3r V_s{}^{\text{local}}(\mathbf{r})+C_0+A_0, \tag{I.7}$$

where $V_s{}^{\text{local}}$ denotes the local part of the pseudopotential and C_0 and A_0 result from C and A, respectively, for $\Delta V_s\equiv V_s-\langle V_s\rangle=0$, we get

$$G'(\mathbf{p},\mathbf{q};p_0)=G_0(\mathbf{p},p_0)\delta_{\mathbf{p},\mathbf{q}}+\int\frac{dq_0}{2\pi}G_0(\mathbf{p},p_0)$$
$$\times T(\mathbf{p},\mathbf{q};q_0)G_0(q,p_0-q_0). \tag{I.8}$$

G_0 is obtained from Eq. (I.3) by replacing $H+V_R$ with H_0. The t matrix $T(\mathbf{p},\mathbf{q};q_0)$ contains all information about the scattering of the valence electrons by the lattice ions and reflects the lattice configuration. To make the dependence of T on the lattice configuration more explicit, ΔH is split into

$$\Delta H=\sum_l\Delta H_l, \tag{I.9}$$

where ΔH_l is the contribution to ΔH due to the ion l. The scattering matrix T can then be written in terms of the scattering matrix t_l, describing the scattering of the valence electrons by ΔH_l, putting $\Delta H_{l'}=0$, with $l'\neq l$, as follows:

$$T(\mathbf{p},\mathbf{q};q_0)=\sum_l T_l(\mathbf{p},\mathbf{q};q_0), \tag{I.10}$$

with

$$T_l(\mathbf{p},\mathbf{q};q_0)=e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_l}t_l(\mathbf{p},\mathbf{q};q_0)+\sum_{l'\neq l}\int e^{i[(\lambda-\mathbf{p})\cdot\mathbf{r}_l+(\mathbf{q}-\lambda)\cdot\mathbf{r}_{l'}]}\cdot t_l(\mathbf{p},\lambda;q_0)$$

$$\times G_0(\lambda,q_0)t_l(\lambda,\mathbf{q};q_0)\frac{d^3\lambda}{(2\pi)^3}+\sum_{\substack{l',l''\\(l'\neq l,l'\neq l'')}}\int\int e^{i[(\lambda-\mathbf{p})\cdot\mathbf{r}_l+(\sigma-\lambda)\cdot\mathbf{r}_{l'}+(\mathbf{q}-\sigma)\cdot\mathbf{r}_{l''}]}$$

$$\times t_l(\mathbf{p},\lambda;q_0)G_0(\lambda,q_0)t_{l'}(\lambda,\sigma;q_0)G_0(\sigma,q_0)t_{l''}(\sigma,\mathbf{q};q_0)\frac{d^3\lambda}{(2\pi)^3}\frac{d^3\sigma}{(2\pi)^3}+\cdots. \tag{I.11}$$

[1] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[2] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).
[3] K. H. Bennemann, Phys. Rev. **133**, A1045 (1964).

The scattering matrices t_l are approximately independent of the ionic positions. The higher terms in Eq. (I.11) result from multiple scattering. Under certain conditions the multiple-scattering terms in Eq. (I.11) can be partially summed up.[3] However, it may be noted that multiple scattering can be treated more elegantly and directly by solving in closed form the integral equation for T_l symbolically given by $T_l = \Delta H_l + G_0 T_l \Delta H$. If $\Delta H_l(\mathbf{R}_l)$ is a smoothly varying function with respect to $\mathbf{R}_l$, and for simplicity is assumed to be independent of l, one derives approximately

$$T_l(\mathbf{q,k}; k_0) = \left[\Delta H_l(\mathbf{q,k}) + \int \frac{d^3p}{(2\pi)^3} \Delta H_l(\mathbf{q,p}) \Delta H_l(\mathbf{p,k}) G_0(\mathbf{p},k_0) c_l(\mathbf{p,q}) \right]$$

$$\times \left[1 - \int\int \frac{d^3p}{(2\pi)^3} \frac{d^3s}{(2\pi)^3} \Delta H_l(\mathbf{s,p}) \Delta H_l(\mathbf{p,s}) G_0(\mathbf{p},k_0) G_0(\mathbf{s},k_0) c_l(\mathbf{p,s}) c_l(\mathbf{s,p}) \right]^{-1}. \quad \text{(I.12)}$$

The ion-ion correlation function $c_l(\mathbf{p,q})$ is given by

$$c_l(\mathbf{p,q}) \equiv \sum_{l'} e^{i(\mathbf{q-p}) \cdot \mathbf{r}_{ll'}}. \quad \text{(I.13)}$$

Eq. (I.12) gives an exact result if the perturbing potentials ΔH_l are nonlocal and separable. If ΔH_l is merely a smoothly varying function with respect to R_l, then T_l is expanded in spherical harmonics and the resulting radial functions $(T_l)_{gm}$ are determined similarly to T_l. The integral equation for $t_l(\mathbf{q,k}; k_0)$ is similarly solved. Then t_l is given by Eq. (I.12) with the ion-ion correlation functions replaced by 1.

II. VALENCE-ELECTRON DENSITY

Using Eqs. (I.9) and (I.11) and expanding the valence-electron density $\rho(\mathbf{r})$ in a Fourier series one gets

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}, \quad \text{(II.1)}$$

with

$$\rho_{\mathbf{K}} = \rho_{\mathbf{K}}' + \rho_{\mathbf{K}}'' + \rho_{\mathbf{K}}'''. \quad \text{(II.2)}$$

$\rho_{\mathbf{K}}'$ results from G'' and gives in lowest order no local crystal-field corrections contributing to covalent bonding. It is

$$\rho_{\mathbf{K}}' = \int\int d^3r \frac{dk_0}{2\pi} G''(\mathbf{r,r}; k_0) e^{-i\mathbf{K} \cdot \mathbf{r}}. \quad \text{(II.3)}$$

$\rho_{\mathbf{K}}''$ is given by

$$\rho_{\mathbf{K}}'' = S_{\mathbf{K}} \int \frac{dp_0}{2\pi} \int \frac{d^3p}{(2\pi)^3} G_0(\mathbf{p},p_0) G_0(\mathbf{p-K}, p_0) \left\{ t_{l_0}(\mathbf{p, p-K}; p_0) \right.$$

$$\left. - \int \frac{d^3\lambda}{(2\pi)^3} t_{l_0}(\mathbf{p,\lambda}; p_0) t_{l_0}(\mathbf{\lambda, p-K}; p_0) G_0(\mathbf{\lambda},p_0) - \cdots \right\}. \quad \text{(II.4)}$$

l_0 denotes any lattice ion. $S_{\mathbf{K}}$ is the crystal structure factor:

$$S_{\mathbf{K}} \equiv (1/\Omega) \sum_l e^{-i\mathbf{K} \cdot \mathbf{r}_l}. \quad \text{(II.5)}$$

Averaging the t matrices with respect to p_0 and approximating ΔH_l by a local potential, Eq. (II.4) can be rewritten as

$$\rho_{\mathbf{K}}'' = S_{\mathbf{K}} \left\{ \frac{K^2}{4\pi e^2} [\epsilon(K,0) - 1] t_{l_0}(\mathbf{K}) - \int \frac{d^3\lambda}{(2\pi)^3} F(\mathbf{K,\lambda}) t_{l_0}(\mathbf{\lambda}) t_{l_0}(\mathbf{K-\lambda}) + \cdots \right\}, \quad \text{(II.6)}$$

with

$$F(\mathbf{K,\lambda}) \equiv \int \frac{dp_0}{2\pi} \int \frac{d^3p}{(2\pi)^3} G_0(\mathbf{p+K}, p_0) G_0(\mathbf{p},p_0) G_0(\mathbf{p+\lambda}, p_0). \quad \text{(II.7)}$$

$\epsilon(K,0)$ designates the static dielectric function of a uniform electron gas.[4]

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[4] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).

$\rho_K{}'''$ arises from multiple scattering of the valence electrons and is given by

$$\rho_K{}'''=\sum_{K'}\int\int\frac{dp_0}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}G_0(\mathbf{p},p_0)G_0(\mathbf{p}-\mathbf{K},\,p_0)G_0(\mathbf{p}-\mathbf{K'},\,p_0)$$

$$\times\left\{S_{K'}S_{K-K'}\left(t_{l_0}(\mathbf{p},\,\mathbf{p}-\mathbf{K'};\,p_0)t_{l_0}(\mathbf{p}-\mathbf{K'},\,\mathbf{p}-\mathbf{K};\,p_0)-\int\frac{d^3\lambda}{(2\pi)^3}\right.\right.$$

$$\times G_0(\lambda,p_0)[t_{l_0}(\mathbf{p},\lambda;\,p_0)t_{l_0}(\lambda,\,\mathbf{p}-\mathbf{K'};\,p_0)t_{l_0}(\mathbf{p}-\mathbf{K'},\,\mathbf{p}-\mathbf{K};\,p_0)$$

$$+t_{l_0}(\mathbf{p}-\mathbf{K'},\,\lambda;\,p_0)t_{l_0}(\lambda,\,\mathbf{p}-\mathbf{K};\,p_0)t_{l_0}(\mathbf{p},\,\mathbf{p}-\mathbf{K'};\,p_0)]\right)$$

$$+\sum_{K''}S_{K'}S_{K''}S_{K-K'-K''}G_0(\mathbf{p}-\mathbf{K'}-\mathbf{K''},\,p_0)t_{l_0}(\mathbf{p},\mathbf{p}-\mathbf{K'};\,p_0)$$

$$\left.\times t_{l_0}(\mathbf{p}-\mathbf{K'},\,\mathbf{p}-\mathbf{K'}-\mathbf{K''};\,p_0)t_{l_0}(\mathbf{p}-\mathbf{K'}-\mathbf{K''},\,\mathbf{p}-\mathbf{K};\,p_0)+\cdots\right\}.\quad\text{(II.8)}$$

Using the same approximations as in deriving Eq. (II.6) one gets

$$\rho_K{}'''=\sum_{K'}S_{K'}S_{K-K'}\left(F(\mathbf{K},\mathbf{K'})t_{l_0}(\mathbf{K'})t_{l_0}(\mathbf{K}-\mathbf{K'})-\int R(\mathbf{K},\mathbf{K'},\lambda)[t_{l_0}(\lambda)t_{l_0}(\mathbf{K'}-\lambda)t_{l_0}(\mathbf{K}-\mathbf{K'})\right.$$

$$+t_{l_0}(\lambda-\mathbf{K'})t_{l_0}(\mathbf{K}-\lambda)t_{l_0}(\mathbf{K'})+\cdots]\frac{d^3\lambda}{(2\pi)^3}\Big)+\sum_{K',K''}S_{K'}S_{K''}S_{K-K'-K''}R(\mathbf{K},\mathbf{K'},\mathbf{K'}+\mathbf{K''})$$

$$\times t_{l_0}(\mathbf{K'})t_{l_0}(\mathbf{K''})t_{l_0}(\mathbf{K}-\mathbf{K'}-\mathbf{K''})+\cdots,\quad\text{(II.9)}$$

$$R(\mathbf{K},\mathbf{K'},\lambda)\equiv\int\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}G_0(\mathbf{p},p_0)G_0(\mathbf{p}-\mathbf{K},\,p_0)G_0(\mathbf{p}-\mathbf{K'},\,p_0)G_0(\mathbf{p}-\lambda,\,p_0).\quad\text{(II.10)}$$

By use of these formulas, some Fourier coefficients ρ_K of the valence electron density in diamond are calculated. $\Delta H_l(\mathbf{q})$ is determined using earlier results obtained by Herman[5] and Kleinman and Phillips.[6] The scattering matrix $t_l(\mathbf{q},\mathbf{k};k_0)$ is expanded in Legendre polynomials and then the resulting radial part of $t_l(\mathbf{q})$ is determined as mentioned earlier. The obtained results for ρ_K are given in Table I.

TABLE I. Fourier coefficients ρ_K of valence-electron charge density in diamond, given in units of electrons per atom. Column 2 presents the results following from the approximation $T=\sum_l\cdot\Delta H_l$ and neglecting ρ_K'. In Column 3 the results of the previous column are corrected by taking into account ρ_K'. Column 4 results from $T_l\cong t_l$. Column 5 results from $T_l=t_l+\sum_{l'\neq l}t_lG_0t_{l'}+\cdots$.

(1) $(a/2\pi)\mathbf{K}$	(2) ρ_K	(3) ρ_K	(4) ρ_K	(5) ρ_K
(1,1,1)	1.14	1.09	0.81	0.91
(2,2,0)	0.43	0.37	0.19	0.12
(3,1,1)	0.10	0.09	0.05	−0.10
(2,2,2)	0	0	0	−0.13
(4,0,0)	0.05	0.02	0.02	−0.11

Then, the results given in Table I are used to estimate the number of electrons $n_{c.b.}$ located in a covalent bond in diamond. It is

$$n_{c.b.}=2\int_{\Omega/2}\rho(\mathbf{x})d^3x,\quad\text{(II.11)}$$

where Ω denotes the volume of the region around the [111] axis between two nearest-neighbor lattice atoms in which the covalent bonding charge is presumably located. For symmetry reasons $\frac{1}{2}\Omega$ is approximately given by $\frac{1}{8}\Omega_0$, where Ω_0 is the volume of the atomic cell. One finds that 1.2 electrons are approximately located in a covalent bond in diamond.

The valence-electron density along the [111] axis is studied in detail in Figs. 1, 2, 3, and 4.[7] Figs. 1, 2, and 3 display the significance of the approximations $T_l\cong\Delta H_l$, and $T_l\cong t_l$, and the importance of the higher Fourier coefficients ρ_K, which are strongly affected by multiple scattering. Fig. 4 shows the total contribution to the valence-electron charge density along the [111] axis due to multiple scattering.

[5] F. Herman, Phys. Rev. 88, 1210 (1952).
[6] L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959).
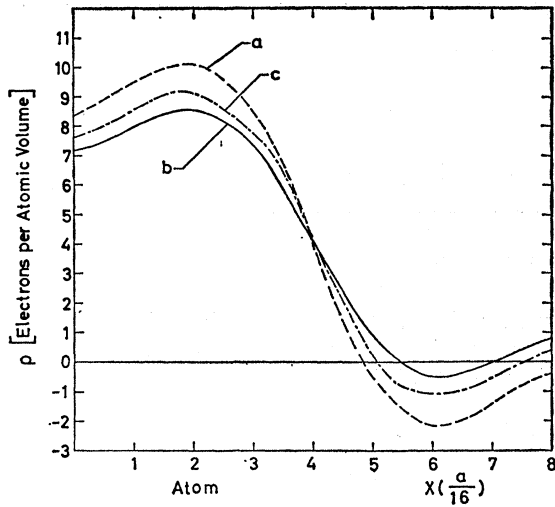[7] L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).

Fig. 1. Valence-electron charge density along a [111] axis in diamond as resulting from ρ_0 and $\rho\langle 111 \rangle$. Curve "a" results from approximating the scattering matrix T_l by ΔH_l, curve "b" from $T_l \cong t_l$, and curve "c" from $T_l \cong t_l + \Sigma_{l \neq l'} t_l G_0 t_{l'} + \cdots$.

III. COHESIVE ENERGY

The cohesive energy of diamond is approximately given by

$$E_{\text{coh}} = \tfrac{1}{2}\phi + E_{\text{el}}/N - E_{\text{free atom}}. \quad (\text{III.1})$$

ϕ gives the electrostatic energy of one lattice ion due to the interaction with all other lattice ions and the uniform gas of valence electrons. ϕ is determined using the Ewald method.[8] $E_{\text{free atom}}$ is the energy necessary to remove the four valence electrons from the free atom.
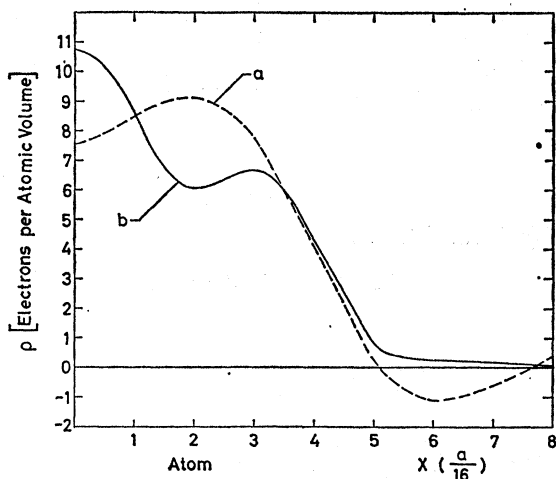

Fig. 2. Valence electron charge density along a [111] axis in diamond obtained by taking into account multiple scattering. Curve "a" results from ρ_0 and $\rho\langle 111 \rangle$. Curve "b" results from ρ_0, $\rho\langle 111 \rangle$, $\rho\langle 220 \rangle$, $\rho\langle 311 \rangle$, $\rho\langle 400 \rangle$, and $\rho\langle 222 \rangle$. Note that the effect of the higher Fourier coefficients ρ_K is to transfer charge from the atomic site at $x=2$ to the region between two nearest-neighbor atoms.

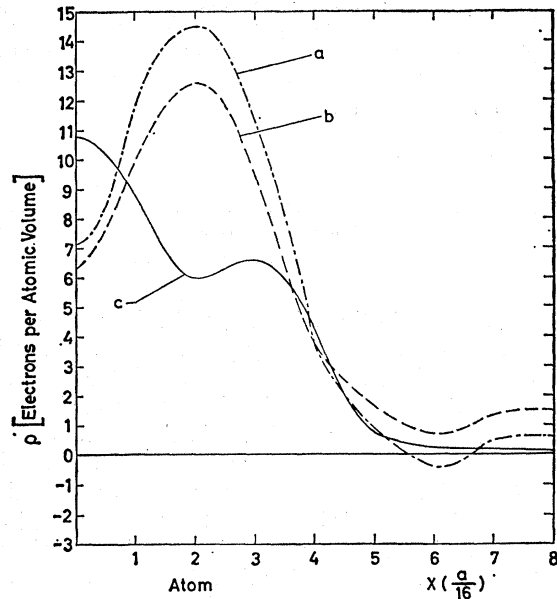[8] K. Fuchs, Proc. Roy. Soc. (London) A151, 585 (1935).

Fig. 3. Valence-electron charge density in diamond resulting from ρ_0, $\rho\langle 111 \rangle$, $\rho\langle 220 \rangle$, $\rho\langle 311 \rangle$, $\rho\langle 400 \rangle$, and $\rho\langle 222 \rangle$. Curve "a" results from $T_l \cong \Delta H_l$, curve "b" from $T_l \cong t_l$, and curve "c" from $T_l = t_l + \Sigma_{l \neq l'} t_l G_0 t_{l'} + \cdots$.

N gives the number of lattice ions. E_{el} is the total energy of the system of valence electrons. It is approximately

$$E_{\text{el}} = NE_0 + N \sum_K E_K, \quad (\text{III.2})$$

with

$$E_0 \equiv 4\{2.21/r_s^2 - 0.916/r_s + E_{\text{corr}} + \langle V_R + A_{\text{iv}} \rangle - \tfrac{1}{2}\langle V_i + C \rangle\}, \quad (\text{III.3})$$

and

$$E_K \equiv \rho_K(\Delta V_i^K + \Delta V_R^K \Delta A_{\text{iv}}^K + \tfrac{1}{2}\Delta C_K + \tfrac{1}{2}\Delta A_K)a^3/8, \quad (\text{III.4})$$

where r_s is the radius of the sphere which contains 1
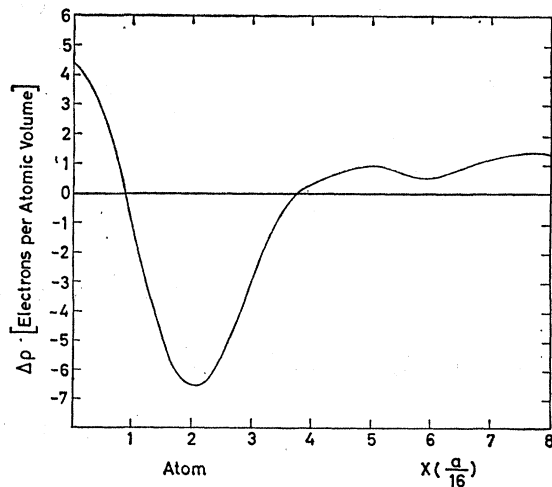

Fig. 4. Contribution $\Delta\rho$ to the valence-electron charge density due to multiple scattering presented by $\Sigma_{l \neq l'} t_l G_0 t_{l'} + \cdots$.

TABLE II. The various contributions to the cohesive energy of diamond are given. All energies are in rydbergs. The value in the 4th column results from neglecting multiple scattering in determining E_K. Column 5 gives the cohesive energy if multiple-electron scattering is neglected. Columns 6 and 7 result from taking into account multiple-electron scattering.

(1) $\dfrac{\phi}{2}$	(2) $E_{\text{free atom}}$	(3) E_0	(4) $\sum\limits_K E_K$ $(T_l \cong t_l)$	(5) E_{coh}	(6) $\sum\limits_K E_K$ $(T_l = t_l + \sum\limits_{l \neq l'} t_l G_0 t_{l'} + \cdots)$	(7) E_{coh}	(8) $E_{\text{coh}}^{\text{exp}}$
-6.45	-11.29	1.03	-6.02	-0.15	-6.32	-0.45	-0.54

valence electron in the uniform gas of valence electrons, E_{corr} is the correlation energy per valence electron in the uniform sea of valence electrons, and A_{IV} describes the interaction between the tightly bound core electrons and the valence electrons a is the lattice constant.

In order to obtain good agreement between the experimental and theoretical value for the cohesive energy of diamond it is important to determine $\langle V_i + C \rangle$ carefully and not to use for this quantity $-\frac{2}{3}E_F$ resulting from the approximation $t_l \cong \Delta H_l$. E_F is the Fermi energy. Thus $\Delta C_l(\mathbf{q})$ needs to be determined. It is

$$\Delta C_l(\mathbf{q}) = -2iv(\mathbf{q}) \int \int \frac{dp_0}{2\pi} \frac{d^3p}{(2\pi)^3}$$

$$\times G_0(\mathbf{p}, p_0) G_0(\mathbf{p}+\mathbf{q}, p_0) t_l(\mathbf{p}+\mathbf{q}, \mathbf{p}; p_0), \quad \text{(III.5)}$$

where $v(\mathbf{q})$ denotes the electron-electron interaction. Averaging t_l with respect to p_0 and approximating ΔH_l by a local potential, one obtains approximately

$$\Delta C_l(\mathbf{q}) = -[\epsilon(q,0) - 1] t_l(\mathbf{q}). \quad \text{(III.6)}$$

This yields

$$\langle V_i + C \rangle = \lim_{q \to 0} \{ V_i(\mathbf{q}) - [\epsilon(\mathbf{q},0) - 1] t_{l_0}(\mathbf{q}) \}. \quad \text{(III.7)}$$

t_l is approximately given by

$$t_l(\mathbf{q}) = \Delta H_l(\mathbf{q}) D(\mathbf{q}), \quad \text{(III.8)}$$

with

$$D(\mathbf{q}) \left\langle \left(1 + \left\langle \int \frac{d^3p}{(2\pi)^3} G_0(\mathbf{p}, k_0) \Delta H_{l_0}(\mathbf{k}+\mathbf{q}, \mathbf{p}) \right\rangle_{\mathbf{k}} \right) \right.$$

$$\times \left(1 - \int \int \frac{d^3p}{(2\pi)^3} \frac{d^3s}{(2\pi)^3} |\Delta H_{l_0}(\mathbf{s})|^2 \right.$$

$$\left. \left. \times G_0(\mathbf{p}+\mathbf{s}, k_0) G_0(\mathbf{s}, k_0) \right)^{-1} \right\rangle_{k_0}. \quad \text{(III.9)}$$

Then Eq. (III.7) can be written as

$$\langle V_i + C \rangle = \lim_{q \to 0} \frac{V_i(\mathbf{q})}{1 + D(\mathbf{q})[\epsilon(\mathbf{q},0) - 1]}. \quad \text{(III.10)}$$

The various contributions to the cohesive energy are given in Table II. The used ionization energies are

given by Slater. It becomes obvious that the binding energy resulting from multiple electron scattering plays an important role in the cohesion of diamond.

IV. CRYSTAL POTENTIAL IN TERMS OF MULTIPOLE FIELDS

It is useful for many studies, for example of optical properties of the crystal, to expand the total crystal field $V(\mathbf{r})$ which a valence electron feels in terms of the Coulomb field due to spherically symmetrically distributed charges around each lattice side, dipole fields, and higher multipole fields. The multipole fields are a consequence of the lack of spherical symmetry of the valence-electron charge distribution within the elementary cell of the crystal or the atomic cell. It is clear that the multipole fields become more and more important as we go from metals to crystals with strong covalent bonding.

The crystal is divided into atomic cells of volume Ω_0 defined by

$$\Omega_0 = \Omega/N. \quad \text{(IV.1)}$$

For simplicity we work within the Hartree approximation and assume a spherically symmetrical charge distribution of the tightly bound core electrons. Then the multipole fields are contained in $\Delta C(\mathbf{r})$,

$$\Delta C(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'. \quad \text{(IV.2)}$$

$\Delta C(r)$ is rewritten as

$$\Delta C(\mathbf{r}) = \sum_j \Delta C_j(\mathbf{r} - \mathbf{r}_j), \quad \text{(IV.3)}$$

with

$$\Delta C_j(\mathbf{r} - \mathbf{r}_j) \equiv \int_{\Omega_0} d^3 r' \frac{\rho(\mathbf{r}' - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}'|}. \quad \text{(IV.4)}$$

Then, approximating Ω_0 by a sphere and expanding the integrand in Eq. (IV.4) in terms of spherical harmonics, one gets

$$\Delta C_j(\mathbf{r} - \mathbf{r}_j) = \sum_{g=0}^{\infty} M_g(r_0, (\mathbf{R}_j/R_j)) R_j^{-g-1},$$

$$\mathbf{R}_j \equiv \mathbf{r} - \mathbf{r}_j > r_0, \quad \text{(IV.5)}$$

where r_0 is the radius of the sphere with volume Ω_0.

The moments M_g are defined as

$$M_g(r_0, \mathbf{R}_j/R_j) \equiv 4\pi \sum_{\mathbf{K}} i^g J_g(\mathbf{K}, r_0) \rho_{\mathbf{K}} P_g(\vartheta_{\mathbf{K},\mathbf{R}_j}), \quad \text{(IV.6)}$$

with

$$J_g(\mathbf{K}, r_0) \equiv \frac{1}{K^{g+1}} \int_0^{K r_0} dy \, y^g j_g(y), \quad \text{(IV.7)}$$

where j_g are spherical Bessel functions.
J_g can readily be evaluated for the most important small g values. If $R_j < r_0$, one gets

$$\Delta C_j(\mathbf{R}_j) = \sum_{g=0}^{\infty} [M_g(R_j, \mathbf{R}_j/R_j) R_j^{-g-1}$$
$$+ Q_g(r_0, \mathbf{R}_j) R_j{}^g], \quad \text{(IV.8)}$$

with

$$Q_g(r_0, \mathbf{R}_j) \equiv 4\pi i^g \sum_{K \neq 0} \rho_{\mathbf{K}} \cdot P_g(\vartheta_{\mathbf{K},\mathbf{R}_j})$$
$$\times \int_{R_j}^{r_0} dy \, y^{-g-1} j_g(Ky). \quad \text{(IV.9)}$$

Note that the functions M_g and Q_g can be readily determined, provided the $\rho_{\mathbf{K}}$ are known.

Using for example the Slater approximation for the exchange potential, it is easily possible also to expand the crystal field in terms of multipole fields within the Hartree-Fock approximation.

V. NEW METHOD FOR DETERMINING LATTICE FORCE CONSTANTS

Using Eqs. (I.3), (I.8), and (I.10) the total energy of the system of valence electrons can be expressed explicitly in terms of the ionic positions. This is very important for determining the force constants fundamental in lattice dynamics. According to a familiar statistical formula[9] one gets

$$\partial E_{\mathrm{el}}/\partial \mathbf{r}_j = \langle (\partial/\partial \mathbf{r}_j) H \rangle, \quad \text{(V.1)}$$

where the average is over the ground state of the system of valence electrons. Eq. (V.1) can approximately be rewritten as

$$\frac{\partial E_{\mathrm{el}}}{\partial \mathbf{r}_j} = -Ze \int \int \int \frac{d^3 p}{(2\pi)^3} \frac{d^3 q}{(2\pi)^3} \frac{dp_0}{2\pi} e^{i(\mathbf{p}-\mathbf{q}) \cdot \mathbf{r}_j}$$
$$\times M(\mathbf{q},\mathbf{p}) G(\mathbf{p},\mathbf{q}; p_0), \quad \text{(V.2)}$$

with

$$M(\mathbf{q},\mathbf{p}) \equiv \left\langle \mathbf{q} \left| \frac{\mathbf{r}}{r^3} \right| \mathbf{p} \right\rangle + \sum_{t,t'} b_t{}^j(\mathbf{p}) b_{t'}{}^{j*}(\mathbf{q})$$
$$\times \left\langle \varphi_{t'}{}^j(\mathbf{r}) \left| \frac{\mathbf{r}}{r^3} \right| \varphi_t{}^j(\mathbf{r}) \right\rangle + \cdots, \quad \text{(V.3)}$$

$$b_t{}^j(\mathbf{p}) = \langle \varphi_t{}^j(\mathbf{r}) | \mathbf{p} \rangle, \quad \text{(V.4)}$$

where $M(\mathbf{q},\mathbf{p})$ is independent of the ionic positions. It has been assumed for simplicity that the states φ_t are given by a linear combination of nonoverlapping atomic-core states $\varphi_t{}^l$. Further, for the repulsive potential V_R we have taken the form given by Cohen and Heine.[2] Note that Eq. (V.2) can be used for a self-consistent determination of lattice distortion due to lattice defects.

The second derivative of E_{el} with respect to an ionic position yields the lowest order force constants of interest in lattice dynamics. One gets from Eq. (V.2) the expression

$$\frac{\partial E_{\mathrm{el}}}{\partial \mathbf{r}_j \partial \mathbf{r}_i} = -Ze \int \int \int \frac{d^3 p}{(2\pi)^3} \frac{d^3 q}{(2\pi)^3} \frac{dp_0}{2\pi} e^{i(\mathbf{p}-\mathbf{q}) \cdot \mathbf{r}_j} M(\mathbf{q},\mathbf{p}) G_0(\mathbf{p},p_0) G_0(\mathbf{q},p_0) \partial T(\mathbf{p},\mathbf{q}; p_0)/\partial \mathbf{r}_i, \quad i \neq j. \quad \text{(V.5)}$$

The corresponding expression for $i = j$ can most easily be obtained from the familiar sum rule for the lattice force constants of this type. It is

$$\frac{\partial}{\partial \mathbf{r}_i} T(\mathbf{p},\mathbf{q}; p_0) = t_i(\mathbf{p},\mathbf{q}; p_0) \frac{\partial}{\partial \mathbf{r}_i} e^{i(\mathbf{q}-\mathbf{p}) \cdot \mathbf{r}_i} + \int \frac{d^3 \lambda}{(2\pi)^3} \{ \sum_{l \neq i} e^{i(\mathbf{q}-\lambda) \cdot \mathbf{r}_l} t_l(\lambda,\mathbf{q}; p_0) t_i(\mathbf{p},\lambda; p_0) G_0(\lambda,p_0) \partial e^{i(\lambda-\mathbf{p}) \cdot \mathbf{r}_i} / \partial \mathbf{r}_i$$
$$+ \sum_{l \neq i} e^{i(\lambda-\mathbf{p}) \cdot \mathbf{r}_l} t_l(\mathbf{p},\lambda; p_0) t_i(\lambda,\mathbf{q}; p_0) G_0(\lambda,p_0) \partial e^{i(\mathbf{q}-\lambda) \cdot \mathbf{r}_i} / \partial \mathbf{r}_i + \cdots \}. \quad \text{(V.6)}$$

Again, averaging i_l with respect to p_0 and approximating ΔH_l by a local operator, Eq. (V.5) can be rewritten as

$$\frac{\partial E_{\mathrm{el}}}{\partial \mathbf{r}_i \partial \mathbf{r}_j} = -Ze \int \frac{d^3 q}{(2\pi)^3} M(\mathbf{q}) (L(\mathbf{q},\mathbf{r}_i,\mathbf{r}_j) + K(\mathbf{q},\mathbf{r}_i,\mathbf{r}_j)) + \cdots, \quad i \neq j, \quad \text{(V.7)}$$

with

$$L(\mathbf{q},\mathbf{r}_i,\mathbf{r}_j) \equiv i\mathbf{q}v^{-1}(q)[1 - \epsilon(q,0)] t_{l_0}(-\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_{ij}}, \quad \text{(V.8)}$$

[9] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, English transl.: E. Peierls and R. F. Peierls (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958).

and

$$K(\mathbf{q},\mathbf{r}_i,\mathbf{r}_j) \equiv i \sum_{l \neq i} \int \frac{d^3\lambda}{(2\pi)^3} F(\mathbf{q},\lambda) t_{l_0}(\lambda-\mathbf{q}) t_{l_0}(-\lambda)[\lambda e^{i(\mathbf{q}\cdot\mathbf{r}_{lj}+\lambda\cdot\mathbf{r}_{il})}+(\mathbf{q}-\lambda)e^{i(\mathbf{q}\cdot\mathbf{r}_{ij}+\lambda\cdot\mathbf{r}_{li})}]. \tag{V.9}$$

Finally, the function K can be rewritten as

$$K(\mathbf{q},\mathbf{r}_i,\mathbf{r}_j) = i \int \frac{d^3\lambda}{(2\pi)^3} F(\mathbf{q},\lambda) t_{l_0}(\lambda-\mathbf{q}) t_{l_0}(-\lambda)\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} + \sum_{\mathbf{K}} (\mathbf{q}+\mathbf{K})S_{\mathbf{K}}e^{i(\mathbf{q}\cdot\mathbf{r}_{ij}+\mathbf{K}\cdot\mathbf{r}_i)} t_{l_0}(\mathbf{K}) t_{l_0}(-\mathbf{q}-\mathbf{K})$$
$$\times[F[\mathbf{q},\mathbf{q}+\mathbf{K})+F(\mathbf{q},-\mathbf{K})]. \tag{V.10}$$

In the same way higher derivatives of E_{el} with respect to ionic positions can be determined.

VI. CONCLUDING REMARKS

It has been shown how the pseudopotential theory can be extended by using t matrices. The t-matrix approach yields an analytical method for describing covalent bonding in diamond. It has been demonstrated that covalent bonding arises from multiple scattering of the valence electrons by the lattice ions. The theory yields a satisfactory result for the cohesive energy of diamond. A more proper treatment of exchange and residual correlation among the valence electrons will probably improve the agreement between the theoretical and experimental value of the cohesive energy. In a forthcoming paper the cohesive energies of diamond, silicon, and germanium will be studied in great detail.

The t-matrix approach makes it possible to evaluate explicitly the dependence of the energy of the system of valence electrons on the lattice positions of the individual ions. This dependence turns out to be very simple. Thus, it seems that we have a promising direct method in hand to determine lattice force constants.