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Coulomb interactions in semiconductors and insulators

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In tight-binding theory, the electron-electron interaction enters (1) through an intra-atomic repulsion U, which is tabulated for nontransition elements, (2) through an interatomic repulsion e^2/d, and (3) through relaxation effects, which are included through a dielectric constant ϵ. For self-consistent band-structure calculations an effective repulsion $U^* = U - \alpha e^2/d$, with α the Madelung constant, enters. For semiconductors, U^* is ordinarily less than zero, suggesting that Coulomb shifts should be neglected. In insulators, U^* is small compared with U, but not negligible. The photothreshold in covalent solids is predicted to be reduced, in comparison to the tight-binding valence-band maximum, by $U/2$ because of dielectric relaxation. The band gap is predicted to be enhanced, in comparison to tight-binding theory (or density-functional theory) by U/ϵ. Both predictions are in rough accord with experiment. Similar shifts are expected for ionic crystals. The cohesive energy is predicted to be given by the change in the eigenvalues of occupied states, but reduced in homopolar covalent solids by $U^*/(2\epsilon)$ (with a Madelung constant α of unity for this correction). In alkali halides the cohesion is reduced, in comparison to the difference in alkali and halogen free-atom electron energies, by U^* (with the halogen U and the crystalline Madelung constant). In the divalent compounds the cohesion is predicted to be reduced, in comparison to twice the difference in free-atom energy levels, by 3 times the corresponding U^*. The intra-atomic repulsion can also lead to formation of a correlated state, as in the Mott transition. This is treated in the unrestricted Hartree-Fock approximation. A condition on the ratio of the appropriate U^* and the interatomic level coupling V is obtained for the formation of the correlated state, that $(U^*/V)^2$ exceed 4 times the number of coupled nearest neighbors. This is applied also to the ideal silicon (111) surface, confirming that it should be antiferromagnetic. The prevention of buckling of this surface by Coulomb effects is also discussed.

I. COULOMB INTERACTIONS IN TIGHT-BINDING THEORY

The conceptual basis of tight-binding theory is the expansion of the electronic states in terms of atomic orbitals $|i\rangle$; in terms of these the Hamiltonian may be written in second-quantized notation as

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{i,j} V_{ij} c_i^\dagger c_j + \sum_{i,j,k,l} U_{ijkl} c_i^\dagger c_j c_k^\dagger c_l \ . \qquad (1)$$

A. One-electron parameters (Refs. 1 and 2)

Neglect of the final sum (or its approximate inclusion in the first sum) corresponds to a one-electron approximation; the ε_i are atomic-state energies, which we take to be free-atom Hartree-Fock[3] term values, and which are listed in Table I; to the extent that we can neglect the change in atomic orbitals when an electron is removed (neglect relaxation), these are the Hartree-Fock predictions of the free-atom ionization energies.

The V_{ij} are matrix elements between states on neighboring atoms. For these we use universal tight-binding matrix elements given by[2]

$$V_{ll'm} = \eta_{ll'm} \hbar^2 / m d^2 \qquad (2)$$

for nearest neighbors in the solid with l, l', and m the appropriate angular-momentum quantum numbers. This was derived by accommodating the free-electron and tight-binding theory[4] of semiconductors. The geometrical values of $\eta_{ll'm}$ so obtained were adjusted slightly to fit the resulting energy bands of germanium, and taken as universal. The values $\eta_{ss\sigma}$, $\eta_{sp\sigma}$, $\eta_{pp\sigma}$, and $\eta_{pp\pi}$ equal to -1.32, 1.42, 2.22, and -0.63, respectively, result.[2] We shall find shifts in the conduction bands relative to the valence bands due to the repulsion U, and, to be fully consistent, these should have been subtracted from the germanium bands before fitting, but they are sufficiently small (0.47 eV) and the universal parameters sufficiently crude that it is not serious.

B. Electron-electron interactions

The central purpose of the present study is to include the final sum appearing in Eq. (1), representing the Coulomb interaction between electrons, approximately in the theory. This sum includes terms corresponding to a variety of different physical effects; it will be convenient to enumerate them at the outset and see how we may reasonably treat them.

We consider the variety of terms in which all coefficients i, j, k, and l correspond to states on the same atom. First, there are the terms with $i = j = k = l$, which are exactly cancelled by exchange terms in the atomic Hartree-Fock theory which led to the ε_i in Eq. (1). Second, there are terms with $i = j$ and $k = l$, but $j \neq k$. These contribute to the potential used in calculating the ε_i and ε_j. (There are also corresponding exchange terms $i = l$ and $k = j$

TABLE I. Hartree-Fock term values for valence levels (Ref. 3). First entry is $-\varepsilon_s$ and second is $-\varepsilon_p$ (values in parentheses are highest core level). The third entry is U, as determined in the Appendix. All values in eV.

I	II	III	IV	V	VI	VII	VIII	IX	X
							${}_{2}$He	${}_{3}$Li	
							24.98	5.34	
								. . .	
								8.17	
	${}_{4}$Be	${}_{5}$B	${}_{6}$C	${}_{7}$N	${}_{8}$O	${}_{9}$F	${}_{10}$Ne	${}_{11}$Na	
	8.42	13.46	19.38	26.22	34.02	42.79	52.53	4.96	
	5.81[a]	8.43	11.07	13.84	16.77	19.87	23.14	(41.31)	
	10.25	10.26	11.76	13.15	14.47	15.75	17.00	6.17	
	${}_{12}$Mg	${}_{13}$Al	${}_{14}$Si	${}_{15}$P	${}_{16}$S	${}_{17}$Cl	${}_{18}$Ar	${}_{19}$K	${}_{20}$Ca
	6.89	10.71	14.79	19.22	24.02	29.20	34.76	4.01	5.32
	3.79[a]	5.71	7.59	9.54	11.60	13.78	16.08	(25.97)	(36.48)
	7.28	6.63	7.64	8.57	9.45	10.30	11.12	5.56	6.40
${}_{29}$Cu	${}_{30}$Zn	${}_{31}$Ga	${}_{32}$Ge	${}_{33}$As	${}_{34}$Se	${}_{35}$Br	${}_{36}$Kr	${}_{37}$Rb	${}_{38}$Sr
6.49	7.96	11.55	15.16	18.92	22.86	27.01	31.37	3.75	4.86
3.31[a]	3.98[a]	5.67	7.33	8.98	10.68	12.44	14.26	(22.04)	(29.88)
7.07	7.83	6.61	7.51	8.31	9.07	9.78	10.48	5.02	5.71
${}_{47}$Ag	${}_{48}$Cd	${}_{49}$In	${}_{50}$Sn	${}_{51}$Sb	${}_{52}$Te	${}_{53}$I	${}_{54}$Xe	${}_{55}$Cs	${}_{56}$Ba
5.99	7.21	10.14	13.04	16.03	19.12	22.34	25.70	3.37	4.29
3.29[a]	3.89[a]	5.37	6.76	8.14	9.54	10.97	12.44	(18.60)	(24.60)
6.34	6.95	6.00	6.73	7.39	8.00	8.58	9.13	5.05	5.70
${}_{79}$Au	${}_{80}$Hg	${}_{81}$Tl	${}_{82}$Pb	${}_{83}$Bi	${}_{84}$Po	${}_{85}$At	${}_{86}$Rn	${}_{87}$Fr	${}_{88}$Ra
6.01	7.10	9.83	12.49	15.19	17.97	20.83	23.78	3.21	4.05
3.31[a]	3.83[a]	5.24	6.53	7.79	9.05	10.34	11.65	(17.10)	(22.31)
6.75	7.33	6.30	7.03	7.68	8.28	8.85	9.39	4.93	5.54

[a] Values extrapolated from surrounding values.

which contribute to the potential.) If the same states were occupied in the solid as in the atom, these would already be included. If, on the other hand, there was an additional occupied state in the solid (e.g., in a negative Cl ion), there is an additional shift in the eigenvalues, which we may write as U_{ij}. This is the change in the energy eigenvalue for a second electron when the first is added; this corresponds to the Hartree-Fock prediction (again with the neglect of relaxation) of the difference between the first and second ionization potentials (or the difference between the electron affinity and the first ionization potential). Again with the neglect of relaxation corrections, this becomes the Coulomb repulsion between electrons in the two orbitals (minus the exchange attraction). To a reasonable approximation (see the Appendix) it can be taken as the same for all pairs of valence states on the atom. Then we may write it as U and call it *the intra-atomic Coulomb repulsion.* This is the central parameter of our analysis here. We have provided a systematic set for the *sp*-configuration atoms as described in the Appendix, and included them in Table I.

There are also terms with $i=j$, $k\neq l$, etc. which are not included in Hartree-Fock theory; they would modify both the free-atom energies and the ionization potentials, but are appropriately dropped here.

There are also terms involving states on different atoms. First, there are terms with $i=j$ on one atom and $k=l$ on another. This is *the inter-atomic Coulomb repulsion,* the shift in the energy of a state on one atom due to the presence of an electron on the other. To the extent that the states are spherically symmetric and nonoverlapping, it is related to the internuclear distance d by e^2/d, and we make this approximation. If all neighboring atoms are neutral, these terms are cancelled by the potential from the corresponding nuclear charge. We will be interested here, then, only in corrections for charged atoms.

It will frequently be convenient to combine these corrections with the intra-atomic Coulomb repulsion. U was defined to represent the shift in the energy of an electronic state on an atom as another electron is brought to the atom from an infinite distance away. In most applications we will be interested in the shift as other electrons are moved from the neighborhood to the atom in question, and the net shift will be written as an effective Coulomb repulsion U^*. For example, the shift in energy of an atomic state on one member of a diatomic molecule due to the shift of another electron from the second atom a distance d away to the first would be $U^* = U - e^2/d$.

There are also terms with $i \neq j$ on one atom and $k = l$ on the other. These give rise to the distortion of the charge on the first atom due to a charge on the other. This is essentially a dielectric relaxation, and in most cases in the solid it will be included using a static dielectric constant ϵ. In particular, we may think of the atomic state to which an electron is added as a spherical shell of radius $r_{\rm sh}$ defined so that $U = e^2/r_{\rm sh}$ since the electrostatic repulsion between two such charged shells would be this U. The potential arising from such a shell, in the absence of dielectric relaxation is, of course, e^2/r outside the shell, but, with relaxation of the dielectric outside, the potential becomes $e^2/\epsilon r$ and a constant $e^2/\epsilon r_{\rm sh}$ inside. We may calculate the total energy of this relaxed state by, for example, calculating the work done in adding the charge by infinitesimal increments, requiring a total amount of work $e^2/2\epsilon r_{\rm sh}$. This is less than the work required if there were no dielectric medium by what we may call the *relaxation energy,*

$$E_{\rm relax} = U(\epsilon - 1)/2\epsilon \ . \tag{3}$$

Such corrections are quite important in semiconducting systems. Note that they come from the relaxation of the bonds *outside* the region of the two interacting electrons.

Finally, there are terms with $i \neq j$ on one atom and $k \neq l$ on another. These include the dipole-dipole terms which give rise to the van der Waals interaction between atoms which will not be important here and will be neglected. There are also terms, when the atoms overlap each other, with a single state on one atom and the other three on another, or states on three or four atoms, but these will all be neglected here.

C. The relation to density-functional theory

Contemporary theory of the electronic structure of solids is almost universally based upon density-functional theory, and, in particular, on some local-density approximation to it, principally for computational reasons. For tight-binding theory these computational reasons do not exist and we have chosen to base the formulation on the Hartree-Fock approximation. The most important distinction can be seen in the ionization of a neutral atom. In Hartree-Fock theory we have seen that in the absence of relaxation the ionization energy equals the Hartree-Fock term value. In local-density theory the electron is removed continuously and at each stage the derivative of the energy with respect to change in occupation is equal to the eigenvalue at that stage; the ionization energy is approximately equal to the average of the eigenvalues obtained before and after the removal of the electron;[5] this is called a *transition-state* eigenvalue. It will be very useful conceptually to use eigenvalues which can be identified with the atomic ionization energy; atomic transition-state energies would presumably have served as well as the values in Table I that we use.

There is a second important distinction between our treatment of the solid and that of density-functional *or* Hartree-Fock theory. In either of these theories an electron state in the solid is represented by a wave function distributed over all of the atoms in the system so that the removal of one electron from the system causes a negligible shift in the energies of the others and there is negligible relaxation. This leads to Koopmans's theorem:[6] *In Hartree-Fock theory the electronic eigenvalues are equal to the predicted energy it takes to remove an electron from, or add an electron to, the solid.*

This theorem would clearly be inappropriate if the "solid" consisted of atoms with negligible coupling between their atomic orbitals. For an array of silicon atoms, the energy gain in adding an electron to a $3p$ state (the electron affinity) is greater than that in removing one from a $3p$ state (the ionization energy) by U, equal to 7.64 eV according to Table I. (We neglect, for the moment, relaxation.) The removal energy is to be identified with the Hartree-Fock ε_p of Table I, but the electron affinity is not. Density-functional theory can lead to a similar unphysical result. We shall see that it is natural and convenient to include the Coulomb repulsion U in tight-binding theory, although it is not so easy in full band theory, whether it be of Hartree-Fock or density-functional type. We shall also need to include the effects of relaxation, which is accomplished with the use of Eq. (3).

The physics of these contributions—*intra-atomic* and *inter-atomic repulsion,* and *dielectric relaxation*—is quite clear in the tight-binding context. Their effects provide the subject of this paper.

II. SELF-CONSISTENCY IN TIGHT-BINDING ENERGY BANDS

In universal parameter theory the bands were obtained using free-atom term values from Table I. In a polar semiconductor such as GaAs we may expect charge to be transferred from the gallium to the arsenic atom, shifting the values that we use. We consider this problem first.

Placing a fractional number δZ of additional electrons on an arsenic atom increases the energy of other electrons there by $U\,\delta Z$, but when this is simultaneously done for all arsenic atoms with that charge all being taken from the gallium atoms, there is a reduction in energy due to the charge on all neighboring atoms given by the Madelung energy, $-\alpha e^2/d$, where α is the Madelung constant, equal to 1.64 for the zinc-blende structure. Thus for this problem the shift is $U^*\,\delta Z$, with

$$U^* = U - \alpha e^2/d \ . \tag{4}$$

Such a formula applies to both the gallium and arsenic shifts, using the appropriate U from Table I; the δZ's in this case are equal and opposite.

A. Polar semiconductors

For gallium arsenide, with $d = 2.45$ Å, the second term is 9.64 eV, greater than the U value for arsenic (or for gallium) from Table I, giving a negative U^*.

Taken literally, this would mean that transferring electrons to the arsenic levels would lower their energy still further, an unstable situation in which the atoms would be completely ionized. In fact, the meaning is that the atomic states overlap each other so much that the Madelung calculation (which assumes nonoverlapping spherical atomic densities) is not applicable. We take this to mean that *when U^* is found to be negative, Coulomb shifts in the levels are to be neglected.* Thus the use of atomic term values from Table I *was* appropriate in the calculation of bands for covalent semiconductors, as was confirmed empirically by studies of the known bands.[2] The present study confirms that use of free-atom Hartree-Fock term values is appropriate for the tight-binding calculation of energy bands in semiconductors.

B. Ionic crystals

The Madelung constant α equals 1.75 for ionic crystals in the rocksalt structure, and, with $d=2.82$ Å for NaCl, the second term in Eq. (4) becomes 8.94 eV. From Table I we see that for sodium the first term is considerably less than this; U^* should be taken as zero and the free-atom term value is appropriate. This will generally be true for the metallic atoms in ionic crystals. However, for chlorine the first term is 10.31 eV. Again, the two very nearly cancel, with a sufficiently small difference (1.37 eV) that meaningful bands can be obtained for ionic crystals using free-atom term values, as we found earlier.[1]

The difference, however, is not negative nor zero, so we may ask if inclusion of U^* might not improve the predicted bands in ionic crystals. In the simplest tight-binding description of the bands,[1] only *s* states on the metal and *p* states on the nonmetal are included, and the minimum band gap occurs at the center of the Brillouin zone. The symmetry is sufficiently high that the bands at that point become purely *p*- or *s*-like, and with only nearest-neighbor coupling the band gap becomes simply the difference between the nonmetallic *p*-state and metallic *s*-state energies from Table I. This was noted earlier[1] and the gaps predicted in this way were found to be in reasonable accord with experiment,[7] as seen from Table II.

TABLE II. Band gaps for the alkali halides ($M^{\rm I}X^{\rm VII}$) in eV. The first entry was obtained as $\varepsilon_s(M)-\varepsilon_p(X)$ from Table I. Experimental values (Ref. 7) are in parentheses. The third entry is U^*; a complete transfer of an electron to X should decrease the estimate (first entry) by U^*.

	$_{9}$F	$_{17}$Cl	$_{35}$Br	$_{53}$I
$_{3}$Li	14.5	8.4	7.1	5.6
	(13.6)	(9.4)	(7.6)	
	3.2	0.5	0.6	0.7
$_{11}$Na	14.9	8.8	7.5	6.0
	(11.6)	(8.5)	(7.5)	
	4.9	1.3	1.4	1.4
$_{19}$K	15.9	9.8	8.4	7.0
	(10.7)	(8.4)	(7.4)	(6.0)
	6.4	2.3	2.1	2.1
$_{37}$Rb	16.1	10.0	8.7	7.2
	(10.3)	(8.2)	(7.4)	(6.1)
	6.8	2.6	2.5	2.3
$_{55}$Cs	16.5	10.4	9.1	7.6
	(9.9)	(8.3)	(7.3)	(6.2)
		3.2	2.6	2.8

TABLE III. Band gaps for divalent ionic compounds ($A^{\rm II}B^{\rm VI}$) in eV, predicted as for Table II. Experimental values are in parentheses (Ref. 8). The third value is U^* from Eq. (2), the band-gap decrease for transfer of a single electron.

	$_{8}$O	$_{16}$S	$_{34}$Se	$_{52}$Te
$_{12}$Mg	9.8	4.7	3.8	2.7
	(7.8)		(5.6)	(4.7)
	2.5	-0.2	-0.2	
$_{20}$Ca	11.4	6.3	5.4	4.2
	(7.7)	(5.8)	(4.9)	(4.1)
	4.0	0.6	0.5	0.6
$_{38}$Sr	11.9	6.8	5.8	4.7
	(5.8)	(4.8)	(4.4)	(3.7)
	4.7	1.3	1.0	0.8
$_{56}$Ba	12.4	7.3	6.4	5.3
	(5.1)	(3.9)	(3.6)	(3.4)
	5.3	1.6	1.4	1.3

We may now correct these values using the values of U^* obtained from Eq. (4) and U values for the nonmetallic ion from Table I. U^* is obtained immediately for each compound and is listed as the final entry in Table II. If a full electron was transferred from the alkali metal to the halogen, the gap should simply be reduced by U^*. The observed gaps are, in fact, smaller than the difference in term values (except for LiCl and LiBr), and so the corrections are generally of the correct sign and the magnitudes are roughly correct. In most cases the difference is smaller than our U^*, as is appropriate for a partial transfer of charge. It would be reasonable to use this U^* and the inter-atomic coupling, such as that from Eq. (1), to self-consistently calculate the band gap and effective charges. However, this has not yet been done, and perhaps would not be appropriate until one has made a more careful study of the appropriateness of the coupling, Eq. (2), to ionic crystals.

The same comparison can be made for other ionic compounds. In Table III we give the predictions of the band gap for the alkaline-earth chalcogenides obtained by subtracting the term values from Table I, the experimental values,[8] and the value of U^* obtained from Eq. (4). In this case the corrections appear frequently to correspond to a transfer of about one electron, or an effective charge of the ion of about 1.

III. CORRECTIONS TO THE PHOTOTHRESHOLD

Having obtained the energy bands, we may turn to a number of properties of the solid, paying particular attention to the effects of Coulomb interactions. We might initially think that the calculated valence-band maximum should be a prediction of the *photothreshold,* the energy required to remove an electron from the solid, since the valence-band maximum is based directly on the term values which represent the energy required to remove an electron from the atom.[9] We may see immediately that, because of dielectric relaxation, this is not the case. We first consider an atom lying a short distance z outside a solid with a large dielectric constant. The ionization energy may be seen to be reduced by $-e^2/4z$ by proceeding in steps. We first carry the neutral atom to infinity, costing no work against Coulomb forces, use the free-atom ionization energy to remove an electron, and then gain an energy $e^2/4z$ from the image force $(-e^2/4z^2)$ in returning the atom to its initial position near the surface. This reduced energy corresponds more closely to the energy required to remove an electron from the solid than does the free-atom ionization energy.

We may obtain the corresponding value for the solid using the relaxation energy given in Eq. (3). The energy to remove an electron from the solid *would* be predicted to be the tight-binding valence-band maximum if there were no dielectric relaxation. E_{relax} is just the reduction in the required energy because there is dielectric relaxation. For a semiconductor the dielectric constant is sufficiently large that we may take $(\epsilon-1)/\epsilon$ to be equal to 1, and for a compound we should take a weighted value of U for the two components, or we may take the homopolar value. This gives a correction of simply $U/2$, or around 3.7 eV for the semiconductors below the carbon row. This is indeed very close to the value of 3.8 eV which we found empirically[1] for the correction to the valence-band maximum. We have redone that comparison using revised parameters to plot the experimental[1] photothreshold Φ against the tight-binding valence-band maximum $-E_v$ in Fig. 1. We again see a rather constant shift, in this case by some 4.2 eV. There are more detailed corrections which could be made in addition to the estimate of the shift indicated above. One is the upward shift of the bands due to the nonorthogonality of the atomic states. However, there are different levels of approximation at which this can be done, so we leave it that the predicted shift in the photothreshold given by Eq. (3) is in essential agreement with experiment for semiconductors.

The same formula may be applied for ionic crystals. The (optical) dielectric constant is typically 2.5, so that the factor $(\epsilon-1)/\epsilon$ is typically 0.6, but the U associated with the nonmetallic ion is larger, so corrections similar to those for the semiconductor are expected. This has not yet been explored.

One might ask if we should not have made corrections for the relaxation associated with ion displacement as well; that is, if we should not have used the *static* rather than the *optical* dielectric constant for the ionic crystals. The answer is no; the Franck-Condon principle applies in this case (precisely because the relaxation energy is large in comparison to the relevant vibrational quantum, that of an optical mode[10]), so we may say that the ions do not have time to move during the emission process. In contrast, the relaxation energy of Eq. (3) is not large compared to the relevant electronic energy difference, the optical peak energy E_2, which is typically 5 eV.[11] Thus we may say that the electrons do have time to relax.

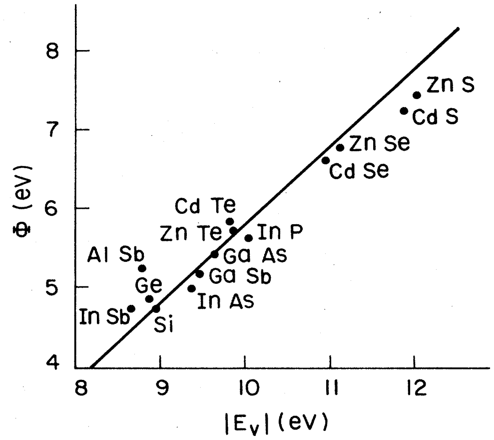

FIG. 1. Experimental photothreshold (compiled in Ref. 1) plotted against the energy of the valence-band maximum obtained in tight-binding theory. Coulomb corrections suggest $\Phi=|E_v|-U/2$, with $U/2$ approximately 3.7 eV; the curve corresponds to this form with $U/2=4.2$ eV.

IV. CORRECTIONS TO THE BAND GAP

The band gap which we obtain from a band-structure calculation corresponds to a bonding-antibonding splitting and is appropriate when we calculate such properties as the dielectric constant; then, an applied field admixes an antibonding state to the bonding state to obtain a dielectric polarization. The bands we obtain are appropriate, just as the atomic term values are when we admix excited states to occupied states in the atom to obtain the atomic polarizability. However, when we actually excite electrons into the conduction band in the semiconductor and separate them from the remaining holes, there is a correction by a U just as if we had taken an electron from one atom among a collection of atoms and placed it upon another atom. Here we have placed an electron in an antibonding state at a site where two electrons already occupied the bond.

We must, however, allow for dielectric relaxation around both the electron and the hole. Both are given by Eq. (3). (If we were distinguishing U values in a compound, one would be that for the anion and one for the cation.) Thus the shift in the gap is $U-2U(\epsilon-1)/2\epsilon$, or

$$\delta E_g = U/\epsilon\ . \tag{5}$$

In a compound, U is to be the average for the constituents.

This is a prediction of the correction to the gaps of density-functional theory, to which attention has recently been drawn by Sham and Schlüter,[12] and Perdew and Levy.[13] Yin[14] has, in fact, given values for this correction

TABLE IV. Predicted enhancement of the gap relative to tight-binding (or local-density) bands, compared with the difference between calculated local-density bands (Refs. 14 and 15) and experiment.

	U/ϵ	Observed
C	2.06	1.37[a]
Si	0.65	0.69[a]
Ge	0.47	0.27[a]
Sn	0.28	
AlP	0.9	0.92[b]
GaAs	0.69	
ZnSe	1.39	
CuBr	2.67	
LiF	6.1	4.7[b]
NaCl	3.5	3.7[b]
CsCl	2.8	3.3[b]
MgO	3.6	2.5[b]
CaS	1.7	2.8[b]
BaS	1.6	2.1[b]
Ne	13.8	9.9[b]
Ar	6.9	6.1[b]
Kr	5.8	4.6[b]

[a] M. T. Yin, Ref. 14.

[b] A. E. Carlsson, Ref. 15.

for diamond, silicon, and germanium by subtracting gaps obtained from self-consistent density-functional theory from experimental gaps. Carlsson[15] has given these values for a number of other systems, including values of 1.36 eV for diamond and 0.62 eV for silicon, consistent with Yin's. These are compared with the predictions from Eq. (5) in Table IV. Our prediction appears to be at least qualitatively correct for a range of materials.

We should distinguish these corrections from the correlation corrections calculated by Horsch, Horsch, and Fulde,[16] who found a *decrease* in gap in diamond due to correlations. This arose from the relaxation of the excited electronic system, analogous to the relaxation effects described above, although theirs seem to be much smaller in magnitude. This presumably is because of a difference in the starting unrelaxed state.

Use of Eq. (5) for ionic solids (with the average U) yielded somewhat larger corrections than for semiconductors, as seen in Table IV, because of their smaller dielectric constant. They are seen in Table IV to be in reasonable accord with observed corrections to density-functional theory. They appear to be of the same origin as corrections estimated by Heaton, Harrison, and Lin,[17] who suggest a band-gap enhancement of some 50% for LiCl.

Adding these corrections to the gaps predicted in Tables II and III would lead to gaps which are too large, but Table IV would indicate that the difficulty is with the tight-binding theory. Comparison is complicated by the uncertainty in the Coulomb corrections discussed in Sec. II B. It has not been explored further.

V. COHESION

To the extent that the system consists of neutral atoms, or that the relevant U^* can be taken to be equal to zero, the change in energy upon formation of the solid, in the context of a self-consistent-field approximation, is given by the change in the sum of eigenvalues for occupied states. In the tight-binding context there are then no double-counting errors; the Coulomb corrections in the solid are cancelled by those in the free atoms. We may see this explicitly for the case of ionic compounds.

A. Ionic solids

The Born[18] theory of cohesion of ionic solids may be followed to give an expression for the cohesion in terms of tight-binding theory. Born imagines starting with, for example, isolated atoms of sodium and chlorine. He then ionizes the sodium atoms, requiring for each an energy which we have identified with the free-atom Hartree-Fock term value ε_s. He then adds each of these electrons to a chlorine atom, gaining the electron affinity, which we have identified with ε_p+U. Then he brings these charged ions together, gaining the Madelung energy, $\alpha e^2/d$, per atom pair. At the conclusion of this process, as the atoms touch each other, there will be some charge redistribution and there will be repulsive interactions $V_0(d)$ which arise largely from the overlap of the sodium core and the chlorine valence states.[19] However, at that point we have already gained almost all of the Madelung electrostatic energy and the repulsion varies so much more rapidly with d than the attractive terms, that at equilibrium it is a small contribution. We write it $6V_0$ for the six nearest sodium neighbors to each chlorine ion. The change in energy per atom pair (the negative of the cohesive energy) is then

$$\begin{aligned} -E_{\text{coh}} &= -\varepsilon_s+\varepsilon_p+U-\alpha e^2/d+6V_0 \\ &= -\varepsilon_s+\varepsilon_p+U^*+6V_0 \ . \end{aligned} \tag{6}$$

Here we see explicitly that if we neglect the effective interaction U^* and the overlap interaction, the energy gain is just the change in energy as the electron is dropped from the sodium to the chlorine state, as we indicated above. The overlap interaction can, in fact, be formulated as the shift in the electron energies due to nonorthogonality of the atomic orbitals, so it is simply a correction to these atomic energies and is included, then, in the change in the sum of individual energies.

In the discussion in Sec. II we found that the band gap was given by the first three terms in the final form of Eq. (6), but with the U^* term proportional to an effective charge transfer, rather than the full charge which is appropriate to the cohesion. Furthermore, the nonorthogonalities which shift the occupied states also shift the empty states, so a different correction than $6V_0$ enters the band gap. Thus it is really only with these two corrections neglected that the cohesion is equal to the band gap as we suggested earlier.[19]

For the specific case of sodium chloride, the first two terms, obtained from Table I, give 8.83 eV. U^* was found in Sec. II to be 1.37 eV, reducing the cohesion to

7.46 eV, to be compared with the observed cohesion of 6.77 eV.[20] We have carried out this evaluation for the other alkali halides, with the results given in Table V. The Coulomb corrections are seen generally to improve the predictions, especially when the uncorrected discrepancies are large. Inclusion of the $6V_0$ would reduce our estimate still further, but the effect of the coupling $V_{sp\sigma}$ between neighbors would increase it.

The corresponding Born theory can be carried out conceptually for the divalent compounds, ignoring the fact that the doubly charged negative ions do not really exist when isolated. We remove, for example, a first electron from calcium at $\varepsilon_s(A)$, with A indicating calcium, and add it to a sulfur atom at $\varepsilon_p(B)+U^*(B)$, with B indicating sulfur. The second electron removed comes from $\varepsilon_s(A)-U^*(A)$ and is placed at $\varepsilon_p(B)+2U^*(B)$. Thus the energy gain is

$$2[\varepsilon_s(A)-\varepsilon_p(B)]-U^*(A)-3U^*(B)\ .$$

Without the U^*'s, the cohesion is twice the term-value difference, approximately twice the gap. Evaluating $U^*(A)$ for the divalent compounds from Eq. (4), we find it to be always negative (and therefore to be dropped), but $U^*(B)$ is positive (except for MgSe and MgTe) and may be multiplied by 3 and subtracted directly to obtain the results compared with experiment in Table VI. The improvement due to the addition of the Coulomb correction is quite remarkable. It is also interesting that in this case the change in the sums of the energies of occupied states would yield a Coulomb correction of $4U^*(B)$ rather than $3U^*(B)$, the difference being essentially a double-counting correction.

It seems to be generally true that tight-binding theory gives quite a good account of the cohesion of ionic solids. The Coulomb correction U^* is not dominant but it *is* sufficiently large to be significant and should be included.

TABLE V. Cohesive energy of the alkali halides ($M^{\mathrm{I}}X^{\mathrm{VII}}$), first as $\varepsilon_s(M)-\varepsilon_p(X)$, and then with U^* [Eq. (4)] subtracted. Experimental values are in parentheses (Ref. 19). All values in eV/atom-pair.

	$_9$F	$_{17}$Cl	$_{35}$Br	$_{53}$I
$_3$Li	14.5	8.4	7.1	5.6
	11.3	7.9	6.5	4.9
	(10.7)	(8.8)	(8.2)	(7.7)
$_{11}$Na	14.9	8.8	7.5	6.0
	10.0	7.5	6.1	4.6
	(7.9)	(6.8)	(6.1)	(5.2)
$_{19}$K	15.9	9.8	8.4	7.0
	9.5	7.5	6.3	4.9
	(7.6)	(6.9)	(6.2)	(5.4)
$_{37}$Rb	16.1	10.0	8.7	7.2
	9.3	7.4	6.2	4.9
	(7.4)	(6.7)	(6.1)	(5.4)

TABLE VI. Cohesive energy of divalent compounds ($A^{\mathrm{II}}B^{\mathrm{VI}}$) predicted as $2[\varepsilon_s(A)-\varepsilon_p(B)]$ per atom pair, and then with $3U^*(B)$ subtracted. Experimental values are in parentheses (Ref. 19). All values in eV/atom-pair.

	$_8$O	$_{16}$S	$_{34}$Se	$_{52}$Te
$_{12}$Mg	19.7	9.4	7.6	5.3
	12.4	9.4	7.6	5.3
	(10.4)	(8.0)		
$_{20}$Ca	22.8	12.6	10.7	8.4
	10.9	10.7	9.0	8.2
	(11.0)	(9.7)	(7.3)	
$_{38}$Sr	23.7	13.5	11.7	9.4
	9.7	9.5	8.7	8.7
	(10.4)	(9.3)		
$_{56}$Ba	24.9	14.6	12.8	10.5
	8.9	10.0	8.5	8.2
	(10.3)	(9.4)	(10.3)	

B. Covalent solids

We have seen that the U^* which enters the band calculation is to be taken equal to zero in the tetrahedral semiconductors. Thus the cohesive energy in the self-consistent-field context is obtained directly by subtracting bond-energy eigenvalues from the starting free-atom electronic energies, and adding the appropriate overlap interaction V_0. This approach gave good results, except for the carbon row, in a recent study of bonding of semiconductors.[21] In diamond, and in the carbon row in general, the simple theory overestimated the cohesion by a factor of about 2, as in the earlier extended-Hückel theory.[22] The reason for the difference between the carbon row and the heavier systems is not clear. It has seemed plausible that it comes from corrections to density-functional theory, called *correlation corrections,* which might be larger for these higher electron densities, but the analysis given below does not support that. It is interesting that a treatment of correlation corrections to the cohesion of diamond by Kiel *et al.*,[23] gave an *increase* in cohesion, with the change in correlation energy accounting for one-quarter of the total cohesion. We shall see why next.

C. Correlation corrections

The Hamiltonian of Eq. (1) allows us to go beyond the self-consistent-field theory of the cohesion. In particular, we formulate the cohesion for a homopolar semiconductor in terms of the energy of independent bonds (as was done in Ref. 21, with corrections for the coupling between bonds). Beginning within the self-consistent-field theory, we write the one-electron bond orbital as an even combination of hybrids, $(|h_1\rangle+|h_2\rangle)/\sqrt{2}$, and with an electron of each spin in a bond state the expectation value of the final term in Eq. (1) is $U/2+e^2/2d$, corresponding to a 50% chance of the electrons being on the same atom and a 50% chance of them being on different atoms. In the free-atom state the two electrons would have always been on different atoms, with an expectation value of the Coulomb term of e^2/d. Thus the bond has an excess Coulomb energy of $U^*/2$ with $U^*=U-e^2/d$. This U^* is *not* negative (because there is no Madelung constant), so the correction $U^*/2$ is a part of self-consistent-field ground-state energy. The values of U^* may be written for diamond, silicon, germanium, and tin, and are 2.41, 1.51, 1.60, and 2.07 eV, respectively.

This correction is ordinarily not included in tight-binding calculations of the cohesion,[21] and was, in fact, omitted in our discussion of the cohesion for covalent solids given above. Indeed it is omitted in any theory in which the potential used for the solid is very close to that for the atom and it was in that spirit that the treatment of covalent solids was made above. Adding it now, to represent the results of self-consistent-field theory, considerably worsens the agreement with experiment, but we may see that terms beyond the self-consistent-field theory—correlation corrections—cancel most of the contribution and restore agreement with experiment.

We shall see later in this section, and more precisely in Sec. VI, that the correlated motion of the two electrons in the bond (intrabond correlation) only reduces the contribution slightly (by perhaps 0.1 eV). However, polarization of the *other* bonds when an extra electron occupies an atom, rather than there being just four on every atom, has a large effect (interband correlation), just as when an electron was excited into an antibond in an occupied bond site as discussed in Sec. IV. The estimate of this effect may not be as convincing as the estimate in Sec. IV, but the same argument suggests that the reduction of both terms in U^* by a factor of approximately $1/\epsilon$ should be appropriate. [It would probably be better to modify the dielectric constant entering by reducing the susceptibility, $\chi=(\epsilon-1)/4\pi$, by a factor of $\frac{3}{4}$ since only three neighboring bonds contribute, but the difference is not large.] Thus the net Coulomb correction to the cohesion is estimated to be $U^*/2\epsilon$. The shift has been largely eliminated and the residual is some 0.2 eV for diamond and near 0.05 eV for the heavier semiconductors.

Subtracting this correction from the tight-binding estimates of the cohesive energy per bond from Ref. 21 slightly improves agreement with experiment for silicon, germanium, and tin; for which we had overestimated the cohesion by some 0.2 eV, but not in an important way. It does little to eliminate the discrepancy of some 3.5 eV for diamond. These are rather crude estimates and perhaps the main message is that the effects appear not to be large on the scale of the accuracy of the theory.

We should note, however, that difference between the $U^*/2\epsilon$ and the $U^*/2$, which is defined to be the correlation correction, *is* large. At about -1.0 eV for diamond, using the values given above, it is close to the -0.9 eV obtained for the change in correlation energy in the formation of diamond by Kiel *et al.*[23] The estimates of cohesion in Ref. 21 succeeded by ignoring both the $U^*/2$ correction and the interband correlation which largely, and quite generally, cancels it.

We may expect a similar cancellation in polar covalent solids and ionic solids. The average shift of the charge between atoms (zero for homopolar semiconductors) is included already in the tight-binding theory and the fluctuations should decrease as the bond polarizability and dielectric constant decrease.

Before proceeding we make a simple estimate of the intrabond correlation. It arises from the final term in the Hamiltonian of Eq. (1) which couples the two-electron bond state to a state in which both electrons are in antibonding states. We shall solve the corresponding problem exactly in the following section, but for the present we note that this coupling is $U^*/2$, and since the antibonding states are each higher in energy by $-2V_2$, where V_2 is the coupling between the two hybrids, with magnitude 4.44 eV in silicon, the energy per bond is lowered by $(U^*)^2/16V_2$, of the order of 0.1 eV and quite negligible.

VI. FORMATION OF A CORRELATED STATE

The Coulomb interaction U can lead to qualitative change in the nature of the electronic state by localizing the electrons on individual atoms when the coupling between the levels on different atoms becomes small. This is called the *Heitler-London transition.* We proceed to the full solution in the tight-binding context.

A. Exact solution for a two-level system

For this simplest two-level problem the final term in Eq. (1) becomes simply

$$U^*(c_{1+}^{\dagger}c_{1+}c_{1-}^{\dagger}c_{1-}+c_{2+}^{\dagger}c_{2+}c_{2-}^{\dagger}c_{2-}) .$$

With two electrons present there are only six possible states, e.g., $c_{1+}^{\dagger}c_{2-}^{\dagger}|0\rangle$. The symmetry is sufficiently high that the two-electron states for this Hamiltonian can be obtained exactly.[24] The ground-state energy, in particular, is found to be

$$E_{\text{tot}}=U^*/2-[(U^*/2)^2+4V_2^2]^{1/2} , \tag{7}$$

where V_2 is the coupling between the two states.

Note first the results indicated in the preceding section. If U^* is neglected, the energy is $2V_2$ (negative), corresponding to two electrons in bond states. Then for small U^*, the Coulomb correction is $U^*/2$, as we found before. The correlation energy which we found in perturbation theory is obtained by expanding the square root in Eq. (7) to second order in U^*, giving the $(-U^*)^2/16V_2$ which we found before.

As U^* becomes large, we may expand the square root in Eq. (7) for small V_2, obtaining $-4V_2^2/U^*$; the $U^*/2$ term has been cancelled. This is in accord with a Heitler-London transition having occurred, so that there is no Coulomb correction proportional to U^*. The origin of the $-4V_2^2/U^*$ term is the coupling of each atomic electronic state to an empty state on the other atom, but higher in energy by U^*, although the direct use of perturbation theory with this one-electron concept gives an estimate a factor of 2 smaller.

An interesting and important feature of Eq. (7) is that the exact energy varies smoothly between the two limits.

The Heitler-London transition, or the formation of a *correlated state,* is continuous in this system. However, it is only the two-level system for which we have the exact solution. For more complex systems, such as the formation of correlated f states in rare-earth metals, which we treated earlier,[24] we need to resort to an approximate solution.

B. Unrestricted Hartree-Fock approximation

For treatment of the rare earths we used an approximation called *unrestricted Hartree-Fock.* In this method, as applied to the two-level system, we again construct one-electron states such as the bond state discussed in Sec. V, but allow the two states to become unsymmetric, $u_1 | h_1 \rangle + u_2 | h_2 \rangle$, with $u_1 \neq u_2$; the states with different spin have u_1 and u_2 interchanged. We then evaluate the expectation value of the Hamiltonian of Eq. (1), and minimize the energy with respect to the variational coefficients u_1 and u_2. It is found[24] that if U^* is less than the magnitude of $2V_2$, the ordinary symmetric bond solution is obtained (with energy $2V_2 + U^*/2$ relative to isolated atoms). However, if U^* is greater than the magnitude of $2V_2$, a second, asymmetric, solution has a lower energy of $-2V_2^2/U^*$. This is also a solution within a self-consistent-field context, but different from the traditional one. We may note that the energy, and, in fact, the derivative of the energy with respect to U^*/V_2, is continuous, but the second derivative is discontinuous. An artificial singularity has been introduced by unrestricted Hartree-Fock theory. The energy of the ground state obtained is always higher than the true energy, and, in fact, has half the magnitude of the exact solution when U^* is very large, as we noted earlier. However, the solution in this region is much better than the simple symmetric bond solution, and the theory is directly applicable to systems other than the two-level system. In particular, it allowed us to discuss the bands and the cohesion of the correlated state in the rare earths and actinides.[24]

It also has an interesting advantage in providing a condition, U^* less than or greater than $-2V_2$, as to whether in the context of self-consistent-field theory we should use traditional symmetric solutions or new symmetry-breaking solutions. Qualitatively different physics and different approximations are suggested in the two regimes. In just this way, it is possible in a real gas-liquid system to go continuously (with appropriate temperature and pressure to take one around the critical point) between the two phases, but quite different approximations are appropriate when we are well within different phases. The distinction is useful even though the criterion is not sharp.

C. Generalization to multiple levels

The generalization of the two-level system to rare earths was quite direct.[24] On each atom there are fourteen f levels (also counting spin orientations). Each is coupled to a band of free-electron states. We allowed Z_f of these levels to have a high probability of occupation and the remaining $14 - Z_f$ to have a low probability of occupation. Then after defining a U^* for the interaction between f electrons on an atom, we obtain a Coulomb shift which is different for the two sets of states and could construct the unrestricted Hartree-Fock problem, and, depending upon the parameters, would find either the usual solution of a partly occupied resonance at the Fermi energy or a split into a full resonance below the Fermi energy and an empty one above, corresponding to a correlated state. This was a generalization from two to fourteen levels; after the Coulomb problem was solved for those fourteen, the coupling between levels on different atoms was included to obtain the bands.

An interesting case of multiple levels in semiconductors might occur for deep impurity levels where U^* can become large. An extreme case is an oxygen impurity, with a large U (14.47 eV), in a semiconductor with a large d (2.36 Å for GaP), for which the effective Coulomb interaction is $U^* = U - e^2/d = 8.36$ eV. Morgan[25] has, in fact, suggested that the optical properties of an oxygen atom substituted for phosphorus in gallium phosphide are best understood in terms of a neutral oxygen configuration and spin multiplets based upon the neighboring gallium hybrids. This deserves a self-consistent analysis using the tight-binding parameters given here, but that has not yet been carried out. It would be interesting, in particular, to see if such a system would form a correlated state, and if so, which of the correlated states (e.g., neutral or charged oxygen) would have the lowest energy.

D. The metal-insulator transition

We may also make a generalization directly to a many-atom system, but retain only a single spin-up and spin-down state on each atom. We consider a simple-cubic arrangement of atoms, each containing an s state, coupled to each of its nearest-neighbor s states of the same spin by $V_{ss\sigma}$. The ordinary energy bands can be written immediately as

$$E(\mathbf{k}) = \varepsilon_s + V_{ss\sigma} f(\mathbf{k}) \,, \tag{8}$$

with

$$f(\mathbf{k}) = 2[\cos(k_x d) + \cos(k_y d) + \cos(k_z d)] \tag{9}$$

for each of the three components of $\mathbf{k}$ running from $-\pi/d$ to $+\pi/d$. If there were a single electron per atom, all states within a planar Fermi surface consisting of the planes bisecting the wave numbers $(\pm 1, \pm 1, \pm 1)\pi/d$ would be occupied. [These are the states with energy $E(\mathbf{k})$ less than ε_s.]

We may also consider a solution with broken symmetry such as that of rocksalt. That structure consists of a simple-cubic arrangement of ions, alternately sodium and chlorine. In the broken-symmetry state in our case, the spin-down occupation on half of the atoms (these might be the Cl sites) exceeds one-half by δZ and the spin-up occupation is less than one-half by δZ, the situation being reversed for the remainder of the atoms (the Na sites). Then the energy of a particular spin state on an atom is shifted by $U^* = U - \alpha e^2/d$ times the occupation of the other spin state on that atom, in this case $\frac{1}{2} \pm \delta Z$. Thus half of the levels (alternate atoms in all directions) have energy $\varepsilon_s + U^*/2 + V_3$ and the other half have energy $\varepsilon_s + U^*/2 - V_3$, with $V_3 = U^* \delta Z$. The solution is again immediate:

$$E(\mathbf{k})=\varepsilon_s+U^*/2\pm\{V_3^2+[f(\mathbf{k})]^2V_{ss\sigma}^2\}^{1/2}\ . \tag{10}$$

We could use a smaller Brillouin zone here or can use the same cubic Brillouin zone as indicated above, taking the negative sign before the square root when $\mathbf{k}$ lies inside the planes bisecting $(\pm1,\pm1,\pm1)\pi/d$ which made up the initial Fermi surface, and the plus sign outside these planes.

We see that a nonzero V_3 opens a gap over the entire Fermi surface for a system with one electron per atom producing an insulator; this is a Mott transition, or, in this case, the formation of an antiferromagnetic insulating state. This special circumstance of planar Fermi surfaces is like a one-dimensional system, and energy would always be gained by forming the correlated state. Adding second-neighbor interactions would warp these surfaces, and a sufficiently small V_3 would leave the system metallic. In that case an integration over occupied states or an approximate evaluation of the energy is necessary to see if the correlated state is to be expected. We shall use an approximation that is appropriate to this more general circumstance, although we continue with the form of the bands given above.

Both the determination of δZ and the total energy require an integration over the occupied states, in this case over the states within the cubic Brillouin zone and the planes bisecting $(\pm1,\pm1,\pm1)\pi/d$; that is, in fact, exactly the face-centered-cubic (or rocksalt) Brillouin zone. A simple way of doing this is the special-point method of Baldereschi,[26] which consists of selecting a representative wave number $\mathbf{k}^*$ in the (face-centered-cubic) Brillouin zone and estimating the average of any quantity as the value at that special wave number. Baldereschi gave methods for selecting such a point, but we have, in fact, shown that the $f(\mathbf{k}^*)$ of Eq. (9) must equal the square root of the number of nearest neighbors, $\sqrt{n}=\sqrt{6}$ in this case.[19] This follows from the requirement that the average energy be given correctly by the formulas also when the coupling is very small compared to V_3, where the result is known from perturbation theory; this result applies much more generally than the rocksalt structure considered here.

If we use the special-point method for both the determination of the average energy, Eq. (10), and the occupation of the individual spin states on each atom, the problem becomes exactly equivalent to the two-level Heitler-London problem treated in subsection A, but with V_2 replaced by $\sqrt{n}\,V_{ss\sigma}$. The condition for the formation of a correlated state is that

$$(U^*)^2\geq 4nV_{ss\sigma}^2\ . \tag{11}$$

If the condition is strongly enough satisfied, we may expect it to be accompanied by a transition to an insulating state, a first-order transition. Our simple antiferromagnetic solution for the ground state is only schematically correct. The criterion is only crudely correct, but may be useful for determining what the general characteristics of some system will be.

E. Application to Si(111)

Allan and Lannoo,[27] and, more recently, Northrup, Ihm, and Cohen,[28] have found that an ideal (111) surface of silicon would be antiferromagnetic. This system is closely related to that discussed above. It consists of a triangular array of dangling bonds, with one electron per bond. Thus we may use a criterion for antiferromagnetism such as Eq. (11), but need values for the parameters.

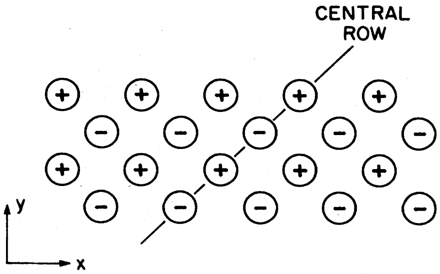

FIG. 2. 2×1 triangular pattern on the dangling hybrids from a (111) surface of silicon. It could represent an antiferromagnetic state on the ideal surface or a buckled pattern; neither appears to occur on the real surface.

The value of U for silicon from Table I is 7.64 eV; we use this for the hybrid. We need the Madelung constant for alternate charges on a triangular lattice as shown in Fig. 2. The edge d' of the individual triangles may be written in terms of the bond length d in the silicon as $d'=2\sqrt{6}d/3$. We first sum the potentials arising from the alternate charges on a central row of surface atoms containing the atom in question, as indicated in Fig. 2. This familiar infinite series yields $(2\ln2)e^2/d'$, and numerical estimates of the contribution of neighboring chains indicates them to be less than a percent of this. We obtain $U^*=U-(\sqrt{6}\ln2)e^2/2d=2.44$ eV.

The coupling between adjacent hybrids in tight-binding theory arises indirectly, through backbonds and antibonds. In fact, the symmetry between bonds and antibonds in the simplest approximations makes these indirect couplings vanish, so we expect that coupling arising from more complete calculations to be very small. This turns out to be true. A surface-band calculation by Appelbaum and Hamann[29] gave a bandwidth, for wave numbers perpendicular to the lines of atoms in Fig. 2, of 0.58 eV. A tight-binding calculation for this plane, with coupling V between hybrids, gives a width of 8 V for this direction. (The phases of four neighbors change from plus to minus along this line.) Thus their result corresponds to a coupling of only 0.07 eV. The special-point method can be used as in the simple-cubic lattice. To find $f(\mathbf{k})$ we imagine V_3 being very large. A particular level with energy $-V_3$ is coupled to two neighbors also with energy $-V_3$, but this does not affect the average energy of these occupied states. It is also coupled to four neighbors at energy $+V_3$, lowering its energy by $-4V^2/2V_3$. For the special-point method to give this result, we obtain $[f(\mathbf{k})]^2=4$. Thus the condition, Eq. (11), for this case becomes $(U^*)^2\geq16V^2$, which, with $U^*=2.44$ and $V=0.07$ eV, is strongly satisfied. We agree with Allan and Lannoo, and with Northrup, Ihm, and Cohen, that the antiferromagnetic state is strongly favored for the ideal Si(111) surface.

F. Surface buckling

Of course, the Si(111) surfaces does not retain an ideal geometry, but undergoes a 2×1 reconstruction. This was long believed to be a simple buckling of the surface, originally suggested by Haneman.[30] This was supposed to be a Jahn-Teller—like effect in which electrons were transferred between dangling hybrids such that half were doubly occupied and half were empty. Then there was a gain in energy linear in displacement as the atoms with occupied hybrids moved outward and those with empty hybrids moved inward. Northrup, Ihm, and Cohen,[28] and Pandey,[31] argued that the Coulomb U^* was too large for this to happen. We may confirm their conclusion using our parameters.

The question concerns dangling hybrids at the silicon surface as described in Ref. 1, pp. 236ff. For the ideal tetrahedral geometry, one might construct sp^3 hybrids oriented toward the nearest neighbors and normal to the surface. However, if the surface atom were displaced outward by a distance u, and hybrids were again constructed with orientation toward the three neighboring subsurface atoms, their sp content would be modified, with the dangling hybrid becoming more s-like and lower in energy, taking, in fact, an energy

$$\varepsilon_h' = \varepsilon_p + (3u + d)^2 V_1 / d^2 \ , \tag{12}$$

with $V_1 = (\varepsilon_s - \varepsilon_p)/4$. [Note that this takes the usual value $(\varepsilon_s + 3\varepsilon_p)/4$ if u equals zero.] The average energy of all four hybrids does not change, and if a single electron occupies the dangling hybrid and a shared electron pair occupied each bond, we would expect a minimum energy near $u = 0$. However, the possibility exists of doubly occupying half of the dangling hybrids, which are displaced outward to lower their energy, and leaving the other half of the dangling hybrids empty; the latter would displace inward to lower the energy of the hybrids in the occupied backbonds. Equation (12) would indicate that the energy should drop linearly in u, while the elastic restoring force should vary quadratically, leading inevitably to a net lowering in energy—a Jahn-Teller effect—and spontaneous lowering of the symmetry of the surface. This seemed to be a natural explanation of an observed 2×1 pattern on the corresponding silicon surface.

To see if such an instability still exists when Coulomb repulsion is included, we may follow the earlier analysis, but now transfer δZ (which may be nonintegral) electrons between a pair of hybrids, letting one atom be displaced outward by u and the other inward by u. The anticipated pattern is that shown in Fig. 2. The gain in energy, for small u, obtained from Eq. (12), is $12uV_1\,\delta Z/d$ per hybrid pair, linear in u as we indicated. The increase in elastic energy was written in terms of a rigidity constant C as $2(\frac{1}{2})C(u/d)^2$. In Ref. 1 the inward and outward displacements were allowed to vary independently and the energy minimized to obtain each. Here we seek only an approximate condition for instability against buckling, and we can let the u for both have the same magnitude. Here, also, we add the Coulomb energy $U^*(\delta Z)^2$ for the pair. Minimizing the total energy with respect to δZ, at fixed u, gives $\delta Z = -6V_1 u/(U^* d)$ and a total energy per pair of $(C - 36V_1^2/U^*)(u/d)^2$.

We see that there is no longer a linear term in the energy and the reconstruction will occur only if the coefficient of $(u/d)^2$ is negative. The condition for reconstruction becomes

$$36V_1^2 > U^*C \ . \tag{13}$$

We now require a value for the parameter C; the value of $U^* = 2.44$ eV found above obtains here also. The constant C was written in terms of the radial force constant C_0 and the angular force constant C_1 in Ref. 1 as $C = C_0/3 + 12C_1$, and two estimates were made, one from the elastic constants and one from the vibration spectra. These are $C = 56.73$ and 29.21 eV, respectively. The inconsistency of the two values reflects the inaccuracy of the simple force-constant model, which may be even greater at the surface.

With the first value of C the condition for buckling is not satisfied; with the other it is. Thus the treatment of *elasticity* is not sufficiently accurate to tell if buckling will occur, but inclusion of the U^* has eliminated the unambiguous prediction of buckling and the results are not inconsistent with the more accurate theories. We expect that Refs. 28 and 31 are correct that there is no buckling, and that the real surface may be the π-bonded—chain model suggested by Pandey.[31]

APPENDIX: PROCEDURE FOR OBTAINING VALUES FOR U

One might estimate U by integrating e^2/r over charge densities obtained from the atomic states, but in the tight-binding context it is better to tune these to fit results of a more complete and accurate calculation or experiment. One atomic quantity directly represented by U is the difference between the first and second ionization potentials. A second possibility would be the difference between the electron affinity and the ionization energy of the atom. One might expect these to have the same value, but changes in the atomic orbitals themselves with changes in occupation make them slightly different. There are also differences in the values, depending upon which atomic states are involved.

Despite these difficulties we seek a systematic set to be used with universal parameter theory. We chose to first calculate U explicitly, using the asymptotic form of the electron density, normalized to one electron,

$$n(r) = (\mu^3/\pi)e^{-2\mu r} \ , \tag{A1}$$

for an atomic state of energy $\varepsilon = -\hbar^2\mu^2/2m$. This yields

$$U = \eta_U e^2 \mu \ , \tag{A2}$$

with $\eta_U = \frac{5}{8}$. A check of this value was made by inserting, for U, the difference between the first and second experimental ionization potentials from Weast,[32] and, for μ, the value obtained from the atomic term value from Table 1. This led to values of μ almost independent of column within each row, even for monovalent and divalent metals for which s-state energies are used. Only for column-VI elements did they differ greatly from other values for the row, presumably because of Hund's-rule energies which are not relevant to the solid. Thus a convenient and reasonable procedure for obtaining a U value appropriate to the difference between first and second ionization potentials is to take the η_U value obtained for the column-

IV element in each row and then deduce U from Eq. (2) for elements from other columns, using μ obtained from the term values of Table I. This was the first procedure to obtain a set of U's. A second procedure was carried out to obtain a U value corresponding to the difference between electron affinity and first ionization potential, but values were available in Weast[32] only for $_6$C, $_8$O, $_9$F, $_{16}$S, $_{17}$Cl, $_{35}$Br, and $_{53}$I. A U value intermediate between those from the first and second procedures would seem appropriate, so in each row we scaled the value from the first procedure by the square root of the ratio, obtained for the halogen in each row, of the values obtained from the first and second procedures. This led finally to values of η_U of 0.479, 0.376, 0.376, 0.351, and 0.373 eV, respectively, for $_6$C, $_{14}$Si, $_{32}$Ge, $_{50}$Sn, and $_{82}$Pb rows, and the U values listed in Table I. (Scaling in the $_{82}$Pb row was taken the same as that in the $_{50}$Sn row. Scaling for $_{11}$Na was taken as for the $_{14}$Si row; for $_{19}$K and $_{20}$Ca as for the $_{32}$Ge row; for $_{37}$Rb and $_{38}$Sr as for the $_{50}$Sn row; and for $_{55}$Cs, $_{56}$Ba, $_{87}$Fr, and $_{88}$Ra as for the $_{82}$Pb row.) U values for columns I, II, IX, and X are based upon the s-state term values. The term values from column I represent a considerably different choice of extrapolation than that in Refs. 1 and 2.

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