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# Unrestricted Hartree-Fock approach to cluster calculations. II. Interaction of cluster and environment

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An *ab initio* approach to determining the appropriate potential in which to embed a cluster in order to simulate a large system is proposed. For ionic and covalent systems, simple approximations are presented as obtained by systematic simplifications of the more general theory. It is also seen that for metallic systems such a reduction is not obtained. The results obtained using the current approach for LiF simulated by a $Li_6F$ cluster are contrasted to those obtained using a more conventional Watson-sphere environment and also free-space boundary conditions.

## I. INTRODUCTION

In the past several years, considerable emphasis has been placed on the study of solid surfaces and on the interaction of absorbates with such surfaces. This interest has arisen for a number of reasons, primarily that surface problems are of considerable scientific and technical interest of themselves. Many of the studies have been implemented by simulating the solid surface by a finite cluster of atoms or ions. Similar work is also being done on bulk systems. An example of a problem of considerable scientific as well as technological interest which is amenable to cluster study would be the relative change in position of energy levels in a semiconductor due to an impurity as a function of whether that impurity is substitutional, interstitial, in the bulk or at a surface. Techniques have evolved to the extent that answering such questions is feasible. A second example which is also of scientific and technological interest concerns the influence of surface defects on chemisorption. In this manuscript we will concentrate upon a subset of the theoretical techniques used for cluster studies. This subset is the proper choice of external potential in which to place the cluster so as to simulate the effect of the remainder of the system.

In this context, a cluster will be defined as a collection of *one* or more atoms, ions, or molecules with *appropriate boundaries* which are studied in some detailed sense for one or more physical properties and is considered by virtue of its boundary conditions to represent this physical property for a larger system such as that of an infinite-solid or a semi-infinite-surface problem. This definition has been problematic in that the nature of the imposed boundaries and the cluster size has been left to the discretion of the person studying the problem. In this manuscript we shall briefly consider some of the formal aspects of these questions.

The cluster by virtue of its finite physical size is from the outset clearly unsuited to describe any physical phenomenon for which the spatial extent of that phenomenon is greater than the physical extent of the cluster in any significant way. Therefore, a study of phenomena involving, say, electrical conductivity or the energy bands of a metal could require a cluster so large as to be impractical from a computational standpoint. Such long range phenomena are better studied using the techniques of energy-band theory. There are phenomena in which the significant physical size of such phenomena are smaller than the spatial extent of the cluster that may be ideal subjects for a cluster simulation. Likely examples of such phenomena include: localized excitations in solids (a tightly bound exciton is a prime example); the formation of self-trapped quasiparticles in a solid (the self-trapped hole or $V_k$ center in an alkali halide is one such system); various properties of point defects or impurities in solids (the $F$ center or electron trapped at a halogen vacancy in an alkali halide is the usual textbook example for such a system[1]); studies related to the formation and breaking of the chemical bond (chemisorption forming our most important example of this).[2]

It is worth stating that due to the inherent size limitations in a cluster simulation, and always assuming, of course, that an accurate model is used to solve for the physical properties, questions of a chemical nature such as bond strength, bond length, and geometrical data in general should be most accurately given by a cluster model. Physical properties such as absorption spectra, photoemission data may be very poorly given unless the optical absorption is a local excitation or in the case of photoemission the finalstate hole remains localized spatially. This should mostly apply to narrow-band materials. In this respect, the proper test of whether or not a cluster model is valid for describing nonlocalized electronic states is *not* whether the cluster has a set of eigenvalues which bear some resemblence to some measured spectrum, but whether or not the cluster electronic structure accurately reproduces the same electronic states calculated using the techniques of energy-band theory assuming, as is necessary, that the same model is used to describe the cluster and the energy-band problem.

It is fortunate that there are at least two available models today for which one has obtained solutions in the band theory limit and in the cluster limit. These are the Hartree-Fock[3] model (HF) and the scattered-wave $X\alpha$ (SW-$X\alpha$) model.[4] The discussion in this paper is given for the HF model but this treatment may be trivially extended to the $X\alpha$ model with identical results.

## II. INTERACTION OF CLUSTER AND ENVIRONMENT

Recently, Marshall, Blint, and Kunz[5] have proposed the use of the unrestricted-Hartree-Fock (UHF) model for solid state cluster simulations. We shall in this paper further develop this application of the UHF technique. It is understood from the outset that the development applies equally well to any other theory which uses an energy functional based on the first-order density matrix or its trace formed from one-particle orbitals. Thus, this derivation is valid for the $X\alpha$ model or the restricted-Hartree-Fock (RHF) model which most authors term the Hartree-Fock model. In this model the many electron Hamiltonian $H$, is

$$H = -\sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i,I}^{n,N} \frac{e^2 Z_I}{|\vec{r}_i - \vec{R}_I|} + \sum_{i>j=1}^{n} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{I>J=1}^{N} \frac{e^2 Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} . \qquad (1)$$

Here upper-case letters refer to nuclear properties, $Z_I$ being the atomic number of the $I$th nucleus at site $R_I$, lower case letters refer to electron properties $\vec{r}_i$ being the location of the $i$th electron and $m$ its mass. The Born-Oppenheimer approximation has been made to eliminate nuclear kinetic energy. In the UHF model the $n$-electron wave function is approximated as

$$\Psi(\vec{x}_i, \cdots, \vec{x}_n) = (n!)^{-1/2} \tilde{A} \pi_i [\phi_i(\vec{x}_i)] . \qquad (2)$$

Where $\tilde{A}$ is the antisymmetrizer, and $\phi$ is a one-electron orbital, and $\vec{x}_i$ includes space variation $r_i$ as well as spin variation $\vec{\sigma}_i$. In the UHF model one forces,

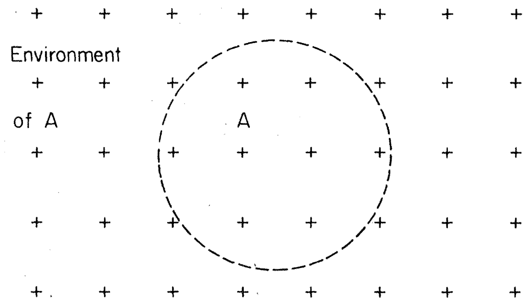

FIG. 1. A schematic of the partitioning of a system into a cluster termed $A$ and the remainder termed the environment of $A$ is given.

$$\phi_i(\vec{x}_i) = \phi_i(\vec{r}_i) \times \begin{cases} \alpha \\ \beta \end{cases}$$
$$\langle i \mid j \rangle = \delta_{ij} . \qquad (3)$$

In this $\alpha$ is an eigenfunction of spin up and $\beta$ for spin down. The form of $\phi_i(\vec{r}_i)$ is otherwise unconstrained. If $\phi_i$ is varied to minimize the expectation value of $H$, the $\phi_i$ are determined by solving

$$F(\rho)\phi_i = \epsilon_i \phi_i$$
$$\rho = \sum_{i=1}^{n} \phi_i(\vec{x}) \phi_i^\dagger(\vec{x}') ,$$
$$F(\rho) = -\frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{e^2 Z_I}{|\vec{r} - \vec{R}_I|} + e^2 \int \frac{\rho(\vec{x}', \vec{x}')}{|\vec{r} - \vec{r}'|} d\vec{x}' - e^2 \rho(\vec{x}, \vec{x}') |\vec{r} - \vec{r}'|^{-1} \hat{P}(\vec{x}', \vec{x}) . \qquad (4)$$

In this formula, $\hat{P}(\vec{x}', \vec{x})$ is the operator which exchanges coordinate $\vec{x}$ with $\vec{x}'$. It is this equation which we would like to solve for the solid as a whole.

Solution of Eqs. (4) for an entire system is often impossible; therefore, we would like to simulate the entire system by a finite cluster. We can see this schematically in Fig. 1. Here the "+" signs refer to nuclear positions and we draw a dotted surface to enclose those nuclei belonging to the cluster. This region is termed $A$ here and the remainder of the system is termed the environment of $A$. The issue at hand is how to partition the system rigorously and what potential or boundary condition to place on $A$ in order to do this rigorously. To effectively carry this out we have recourse to the method of local orbitals of Adams-Gilbert-Kunz.[6-8]

The question of boundary conditions on clusters in general is quite difficult and is not yet completely solved; in fact, we find no general condition at all for metallic systems. The problem arises entirely because a cluster is usually chosen to represent a system which is actually larger in size than the cluster itself. Since clusters are normally smaller than the system represented one should determine, somehow, which conditions to place on the cluster. As a first try, one might try free-space conditions, however for reasons which are quite obvious, this is likely to require a very large cluster to achieve accuracy for either a metal or an ionic solid (the first is due to the diffuse valence orbitals and the second is due to long-range ionic potentials). In the case of a covalent solid, artifacts such as dangling surface bonds may distort results unless a large cluster is used. Therefore, one may expect that a use of free-space boundary conditions is best left to cases where very large clusters may be studied or for studies of molecular crystals, where clusters may be chosen such that neither appreciable covalency, nor long-range potentials occur across the cluster-environment boundary. The appropriate boundary condition to use on a metal is not well defined and often one must use large clusters or be satisfied with qualitative rather than quantative answers. The cases of molecular-bonded systems, ionic systems, or a covalent system are subject to mathematical derivation.

Let us obtain a formal derivation by considering the local-orbital formalism of Adams and Gilbert. Let us use $F$ to represent either the Fock operator for the entire system or a local-density operator. Let $A$ be the region which our cluster occupies, and let $E$ be the remainder (environment of $A$). Then assign $m$ electrons to $A$ (this is chosen to be physically reasonable for the appropriate case, such as the number of electrons on the ions inside $A$ if one has an ionic system). Let

$$F = F_A + U_A, \tag{5}$$

$F_A$ being that part of $F$ which includes kinetic energy, nuclear attraction of the electrons and nuclei inside $A$, and the electron-electron potential including Coulomb and exchange parts for electrons assigned to $A$. Let $W$ be an arbitrary Hermitian operator. We would like to solve,

$$F(\rho)\phi_i = \epsilon_i \phi_i ,$$

with

$$\rho = \sum_{i=\mathrm{occ}} \phi_i \phi_i^\dagger ,$$

but since we wish to study only part of the system, let us solve instead

$$(F_A + U_A - \rho W \rho)\psi_i = \pi_i \psi_i . \tag{6}$$

This is the Adams-Gilbert equation. As they have shown, provided a common $W$ is used for all electrons, one can find

$$\rho = \sum_{i=\mathrm{occ}} \psi_i \psi_i^\dagger \equiv \sum_{i=\mathrm{occ}} \phi_i \phi_j^\dagger , \tag{7}$$

and the $\psi$'s are orthonormal.

First consider an ionic or molecular crystal situation. Let us divide $U_A$ into two parts, $V_A^M$ is an ionic (Madelung) contribution and is long range, and $V_A^S$ is the remainder and is short range. Of course for the molecular system $V^M = 0$. Let $W = V_A^S$. Therefore one solves (using closure) for the occupied orbitals

$$(F_A + V_A^M)\psi_i = \pi_i \psi_i - V_A^S \psi_i + \rho V_A^S \psi_i . \tag{8}$$

Now we are only concerned with the $m$ orbitals of Eq. (23) which lie in $A$. Provided the appropriate number of electrons is assigned to $A$, the solutions found for these electrons should only weakly penetrate $E$.[6,8] Note that $V_A^S$ doesn't penetrate $A$ appreciably and since in the limit of self-consistency $V_A^S \psi_i$ is cancelled by $\rho V_A^S \psi_i$ on the average (true since the eigenvalues of $\rho$ for an occupied orbital is 1). If, for these orbitals, one finds as is reasonable for ionic cases that they don't appreciably penetrate $E$, the appropriate approximate equation including interaction with the remainder of the system is then

$$(F_A + U_A^M)\psi_i = \pi_i \psi_i . \tag{9}$$

From these solution one may calculate the approximate potential-energy surface for an entity wholly in $A$ by evaluating the energy of system $A$ as if it were an isolated system $A$ in a potential field $V_A^M$. One sees that for a molecular bonded system (e.g., Ar) the approximate equation is just the free-space cluster, and for an ionic system the equation includes a Madelung field. In most muffin-tin calculations no such field is used and since at best the Watson sphere potential can simulate the correct Madelung potential at either a cation or an anion, but not both, the information about relative separation of one electron energy levels on differing sites is suspect.

This treatment extends directly to a covalent system. Just as before we envision the system as being composed of ions or molecules here we envision the system as being composed of electrons in bond pairs and ions. Thus for diamond we have a system of $C^{4+}$ and two electron bonds, and on the average, two two-electron bonds per $C^{4+}$ ion. This then proceeds as for the previous case except now we assume the boundary between $A$ and $E$ passes through $n$ two-electron bonds. Since to achieve localization in the Adams-Gilbert sense, we cannot break these bonds, therefore, we must include $n$ more (fewer) electrons in $A$ than a simple atomic view of the system would require and thus $U_A$ has a long range part due to $n$ more (fewer) protons than the atomic view would require and these long range parts are concentrated near the $A$-$E$ interface. From here one solves Eq. (8) for the $n$ more (fewer) electrons, or approximately Eq. (9) for this system using a $V_A^M$ due to the $n$ more (fewer) protons at the boundary. One may recognize here the common expedient of using H atoms to tie off the dangling bonds in a covalent cluster simulation. From this point the other considerations discussed for the ionic situation apply.

This transformation cannot be done in general for metals since the bond behavior of them is such that one cannot simply rotate into a localized representation in a one particle theory.[9] Of course, if the phenomena studied are local in nature despite the metallic host then one is free to proceed. The forming of local bonds to a metal or local magnetism are examples of such phenomena.

The eigenvalues $\pi_i$ of Eq. (8) or the approximate Eq. (9) represent the Koopmans' theorem eigenvalues of the infinite solid $\epsilon_i$ of Eq. (4) only in the limit that the orbital $\phi_i$ in question is localized in $A$ so that in fact $\psi_i$ and $\phi_i$ are identical. Alternately, here the eigenvalues $\pi_i$ may also correspond to an $\epsilon_i$ in the case where the energy band of which $\epsilon_i$ is a part has infinitesimal width as is the case for a core level. For levels $\epsilon_i$ which have finite width, at best the eigenvalues $\pi_i$ represent some state in that band most often near the center of gravity of the band. This property can be easily deduced by using the $\psi_i$ corresponding to the $\epsilon_i$ to generate a Bloch basis set for use in a LCAO band model. Clearly here the one site matrix element of $F$ is $\pi_i$ and using the invariance of the trace of the $F$ matrix under diagonalization, if the overlap of $\psi_i$ into $E$ is small as we assumed, $\pi_i$ must lie near the center of gravity of the band containing $\epsilon_i$.

Similar considerations may be performed to see that chemical data can be realized for atoms included in $A$. Consider the total energy expression. We will partition $\rho$ into two parts, those $\psi_i$ in $A$ and those in $E$, or

$$\rho(\vec{x},\vec{x}') = \sum_i^A \psi_i(\vec{x})\psi_i^\dagger(\vec{x}') + \sum_j^E \psi_j(\vec{x})\,\psi_j^\dagger(\vec{x}'). \tag{10}$$

Here $\sum_i^A$ is orbitals in $A$ and $\sum_j^E$ are for orbitals in $E$. $H$ can be broken apart as

$$H = \sum_i^A \frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^E \frac{\hbar^2}{2m}\nabla_i^2 - e^2\left(\sum_I^A\sum_i^A \frac{Z_I}{|\vec{r}_i-\vec{R}_I|} + \sum_I^E\sum_i^E \frac{Z_I}{|\vec{r}_i-\vec{R}_I|} + \sum_I^A\sum_i^E \frac{Z_I}{|\vec{r}_i-\vec{R}_I|} + \sum_I^E\sum_i^A \frac{Z_I}{|\vec{r}_i-\vec{R}_I|}\right)$$
$$+\left(\frac{e}{2^2}\right)\left(\sum_i^A\sum_j^A \frac{1}{|\vec{r}_i-\vec{r}_j|} + \sum_i^E\sum_j^E \frac{1}{|\vec{r}_i-\vec{r}_j|} + 2\sum_i^E\sum_j^A \frac{1}{|\vec{r}_i-\vec{r}_j|}\right). \tag{11}$$

From here one may proceed in the manner originally derived by Löwdin for ionic solids cohesive energy calculations, to obtain an expression for $E$, the total energy, for our wave function. Here, however, all our orbitals are orthogonal because of our solving a common Hermitian equation and therefore Löwdin's $S$-energy will be absent.[10] The total energy $E$ schematically is

$$E = E_A + E_E + I_{AE}. \tag{12}$$

$E_A$ is the energy of the system of orbitals in $A$ with respect to that part of Eq. (11) which refers only to $A$, $E_E$ is the energy of the system of orbitals in $E$ with respect to that part of Eq. (11) which refers only to $E$, and $I_{AE}$ is the interaction energy of orbitals in $A$ with those in $E$. We assume that only nuclei in $A$ change position and that $A$ is large enough so that the orbitals in $E$ are unchanged by this, or alternatively a Koopmans' like approximation for orbitals in $E$ is made and the orbitals in $E$ are frozen as atoms move in $A$. Thus the term $E_E$ is constant throughout and for convenience since only energy changes are necessary, we neglect $E_E$ hereafter. $E_A$ is simply given and is

$$E_A = \sum_i^A \langle\psi_i| -\frac{\hbar^2}{2m}\nabla^2 - \sum_I^A \frac{e^2 Z_I}{|\vec{r}-\vec{R}_I|}\,|\psi_i\rangle$$
$$+\frac{1}{2}\sum_i^A\sum_j^A\left(\langle\psi_i\,\psi_j|\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\,|\psi_i\,\psi_j\rangle\right.$$
$$\left. - \langle\psi_i\,\psi_j|\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\,|\psi_j\,\psi_i\rangle\right)$$
$$+\frac{1}{2}\sum_I^A\sum_J^A \frac{Z_I Z_j e^2}{|\vec{r}_I-\vec{R}_j|}\,. \tag{13}$$

Thus $E_A$ is the energy of the pseudomolecules in $A$ in the usual Hartree-Fock approximation. Thus only $I_{EA}$ need be evaluated or approximated. It is this term which is evaluated as a cohesive energy by Löwdin, and we may use his results, and any approximation derived therefrom. Then we have,

$$I_{EA} = \sum_I^A\sum_J^E \frac{e^2 Z_I Z_J}{|R_I-R_J|} + \sum_i^A \langle i| - \sum_I^E \frac{Z_I e^2}{|r-R_I|}\,|i\rangle$$
$$+\sum_i^E \langle i| - \sum_I^A \frac{Z_I e^2}{|r-R_I|}\,|i\rangle$$
$$+\sum_i^A\sum_j^E\left(\langle ij|\,\frac{e^2}{|r_1-r_2|}\,|ij\rangle - \langle ij|\,\frac{e^2}{|r_1-r_2|}\,|ji\rangle\right). \tag{14}$$

In principal one should evaluate (14) exactly. However, one may greatly simplify this if one assumes orbitals in $E$ weakly penetrate into $A$ and vice versa. In the extreme limit of no overlap this reduces to a very simple result. Let there be $G_I$ electrons associated with the $I$th nucleus. Then the ionicity, $I_I$ is

$$G_I = Z_I + I_I \,. \tag{15}$$

Then approximately, (14) becomes

$$I_{EA} \cong \sum_I^A \sum_J^E \frac{Z_I Z_j e^2}{|\vec{R}_I - \vec{R}_J|} - \sum_I^A \sum_J^E \frac{G_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} - \sum_I^A \sum_J^E \frac{G_J Z_I e^2}{|\vec{R}_I - \vec{R}_J|} + \sum_I^A \sum_J^E \frac{G_I G_J e^2}{|\vec{R}_I - \vec{R}_J|} + 0.$$

This immediately reduces to

$$I_{EA} \cong \sum_I^A \sum_J^E \frac{I_I I_J e^2}{|\vec{R}_I - \vec{R}_J|} \,. \tag{16}$$

Thus in the lowest approximation the total energy charge for moving a nucleus about in $A$ is given by the energy of a pseudo molecule in $A$ plus a "Madelung" contribution of the atoms in $A$ with those in $E$. Of course, if more precision is needed Eq. (14) may be used or higher order approximation to Eq. (14) may be developed.

## III. EXAMPLE OF LiF

In order to test some of these ideas, a calculation to simulate the electronic energies of LiF solid has been performed. LiF is an ionic solid in a fcc structure. The degree of ionicity is about unity and the system is essentially a collection of $F^-$ and $Li^+$. Here we chose a cluster of six Li ions and one F ion in the center. The Li are octahedrally coordinated with the F ion and thus the cluster is $(Li_6F)^{5+}$. Here we solve Eq. (9) for this system. As a comparison, two other studies are performed. The first is to surround the cluster with a Watson sphere of charge $-5e$ to effect charge neutrality as is often done in SW $X\alpha$ calculations,[2] and the third is to employ simple free-space conditions for the cluster. In forming the Watson sphere, we use a radius of 5.5095 a.u. as is found by having a Watson sphere tangent to the outer surface of a sphere of radius 1.703 a.u. about a Li ion as suggested by a Huggins-Mayer calculation. In any case results are relatively insensitive with small changes in variation of change or radius of the Watson sphere.

The results of this calculation for the one electron eigenvalues and their differences are seen in Table I. There are three salient points to be made from this table. First, the eigenvalues differ greatly from calculation to calculations as one expects due to differing imposed potential. Second, the difference of eigenvalues on a given ion, e.g., $\epsilon(F^-\ 1s) - \epsilon(F^-\ 2s)$ is very insensitive to boundary condition, and finally the difference in eigenvalues on two different ions, e.g., $\epsilon(Li^+\ 1s) - \epsilon(F^-\ 2s)$ is greatly effected by external potential. In the case of two eigenvalues on the same ion the greatest difference between two calculations is about 0.005 eV, whereas for two eigenvalues on different ions the deviation is always greater than 1 eV between the current theory and the other two methods.

TABLE I. The one-electron eigenvalues computed for the $(Li_6F)^{5+}$ cluster are given. The calculations are performed using the *ab initio* external potential discussed in the text and shown in column I; the Watson Sphere potential which yields charge neutrality and shown in column II; and the free space boundary which is shown in column III. Also shown are the differences in energy between each pair of eigenvalue. Results are in eV.

| | I | II | III |
|---|---|---|---|
| $\epsilon(F\ 1s)$ | −712.6993 | −718.3818 | −743.0681 |
| $\epsilon(F\ 2s)$ | −39.9698 | −45.6561 | −70.3407 |
| $\epsilon(F\ 2p)$ | −15.7505 | −21.4378 | −46.1225 |
| $\epsilon(Li\ 1s)$ | −63.6852 | −68.0178 | −92.8108 |
| $\lvert\epsilon(Li\ 1s) - \epsilon(F\ 1s)\rvert$ | 649.0141 | 650.3640 | 650.2573 |
| $\lvert\epsilon(Li\ 1s) - \epsilon(F\ 2p)\rvert$ | 23.7154 | 22.3617 | 22.4701 |
| $\lvert\epsilon(Li\ 1s) - \epsilon(F\ 2p)\rvert$ | 47.9347 | 46.5800 | 46.6883 |
| $\lvert\epsilon(F\ 1s) - \epsilon(F\ 2s)\rvert$ | 672.7295 | 672.7257 | 672.7274 |
| $\lvert\epsilon(F\ 1s) - \epsilon(F\ 2p)\rvert$ | 696.9488 | 696.9440 | 696.9456 |
| $\lvert\epsilon(F\ 2s) - \epsilon(F\ 2p)\rvert$ | 24.2193 | 24.2183 | 24.2182 |

We now argue that this difference is to be expected. A simple argument appropriate for ionic system is as follows. In the limit of the infinite solid the energy of a core level is just that of the free ion plus the Madelung contribution at that ion site to a good approximation. Let $V_M$ be the actual size of the Madelung well. Then for a negative ion the energy eigenvalues $\epsilon_i^-$ is just $\epsilon_{i\,\mathrm{free}}^- - V_M$, and for a positive ion, $\epsilon_i^+$ is just $\epsilon_{i\,\mathrm{free}}^+ + V_M$. Hence to first order, energy differences on the same ion are $\epsilon_i^+ - \epsilon_j^+ = \epsilon_{i\,\mathrm{free}}^+ - \epsilon_{j\,\mathrm{free}}^+$ and $\epsilon_i^- - \epsilon_j^- = \epsilon_{i\,\mathrm{free}}^- - \epsilon_{j\,\mathrm{free}}^-$, and are unaffected by the external potential. Hence the second remark is clearly understood as it relates to Table I. Consider next energy levels on different ions.

Here $\epsilon_i^+ - \epsilon_j^-$ is $\epsilon_{i\,\mathrm{free}}^+ - \epsilon_{j\,\mathrm{free}}^- + 2V_M$. Therefore one must have an external potential reflective of $V_M$ on both types of ion site if this is to be given properly. Clearly the potential used in either Eqs. (8) or (9) satisfies this criterion. However, in the case of the Watson sphere or the free-space boundary condition, this is not so. Since the potential due to a Watson sphere is constant inside it, the difference in ionic potential at a positive-ion site inside to that of a negative-ion site may be rapidly computed for a $(A_6B)^{5I}$ type cubic cluster, where $I$ is the ionicity of $B$ as defined previously. This difference is the same here as for the free-space condition and should be ideally equal to $2V_M$ as previously seen. If $a$ is the length of a cube edge and the system is fcc one finds, if $\Delta$ is the ionic potential difference between positive and negative sites, $\Delta_W = 199.82 I/a$, for a Watson sphere case, whereas the correct Madelung value is $\Delta_M = 190.22 I/a$. Here we assure a fcc system, $I$ the ionicity and $a$ is the cube edge in a.u. (1 a.u. = 0.529 Å) and the energy is in eV. Thus for the $(Li_6F)^{5+}$ case, $\Delta_M$ is 25.13 eV and $\Delta_W$ is 26.28 eV. Thus we predict that the results of the present theory for LiF should differ by 1.25 eV for differences of eigenvalues on positive to negative ion composed to either the Watson sphere case or the free-space case. The difference found in Table I actually range from 1.35 to 1.25 eV and agreement with the simple theory is excellent.

One may conclude that if one wishes accurate values for energy differences for orbitals on different ions as simple Watson sphere is inadequate for ionic system and the error is proportional to the degree of ionicity as seen. Hence for a doubly ionized solid such as TiO or NiO say, the relative error of levels on the anion compared to the cation may be of order 3 eV if a Watson sphere or free space boundary conditions are used.[11-13] In fact this effect may account for the qualitative differences found in the electronic structure of TiO with respect to the relative position of the O $2p$ orbitals and the Ti $3d$ orbitals as seen in the SW-$X\alpha$ cluster calculation using a Watson sphere[11] and the band results where a proper Madelung field is provided.[13] We conclude that in many cases the proper environment potential is simple to include and has non-negligible effects on one electron eigenvalues and should be included.

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[1] W. B. Fowler, *The Physics of Color Centers* (Academic, New York, 1968).

[2] J. C. Slater and K. H. Johnson, Phys. Today 27, 34 (1974).

[3] H. F. Schaeffer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Mass., 1972).

[4] J. C. Slater. *Quantum Theory of Molecules and Solids*, (McGraw-Hill, New York, 1974), Vol. 4.

[5] R. F. Marshall, R. J. Blint, and A. B. Kunz, Solid State Commun. 18, 731 (1976); Phys. Rev. B 13, 3333 (1976).

[6] W. Adams, J. Chem. Phys. 34, 89 (1961).

[7] T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics and Biology*, edited by P. O. Löwdin and B. Pullman (Academic, New York, 1964).

[8] A. Barry Kunz, Phys. Status Solidi 36, 301 (1969).

[9] T. L. Gilbert, Phys. Rev. B 6, 580 (1972).

[10] P. O. Löwdin, Adv. Phys. 5, 1 (1956).

[11] V. A. Gubanov, J. Weber, and J. W. D. Connolly, Chem. Phys. 11, 319 (1975).

[12] K. H. Johnson, R. P. Messmer, and J. W. D. Connolly, Solid State Commun. 12, 313 (1973); R. P. Messmer, C. W. Tucker, Jr., and K. H. Johnson, Surf. Sci. 42, 341 (1974).

[13] D. R. Jennison and A. B. Kunz, Phys. Rev. Lett. 34, 418 (1977).