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Cancellation of Kinetic and Potential Energy in Atoms, Molecules, and Solids*

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In the energy levels of valence electrons in atoms, molecules, solids, and liquids, there is a contribution from the large negative potential energy inside the core of the atom and the large positive kinetic energy which the electron has there. Phillips and Kleinman have shown how the kinetic energy can be represented by a repulsive pseudopotential which cancels most of the potential energy inside the core. The explicit representation of the pseudopotential is now developed further to demonstrate more clearly the extent of the cancellation. The formalism justifies the simple models which are in common use for treating valence electrons. It is also used to relate similar atoms from different rows of the periodic table, and in particular to discuss the systematic trends in the energy levels of the alkali and noble metal atoms.

I. INTRODUCTION

ONE of the most interesting things about valence electrons is the extent to which their observed properties parallel those to be expected from apparently very crude models or simple computational schemes. We have in mind pseudohydrogenic models for atomic energy levels; the point-ion approximation for crystal and ligand fields; the nearly free electron model for metals, alloys, liquid metals, and conjugated aromatic hydrocarbons; and the valence bond scheme for crystal and molecular structures. A common feature of all these models or schemes is that either the core electrons are ignored or their role vastly simplified. Another common feature is that it is not readily apparent from, say, the Hartree-Fock equations that the model should work at all.

Let us take as perhaps the most extreme example the fact that the band structures of metals are remarkably nearly-free-electron-like as regards the form of $E(\mathbf{k})$. There is detailed indirect information about the shapes of the Fermi surfaces in the alkali metals, the interpretation of which[1] also agrees with detailed band structure calculations of Ham.[2] There is detailed direct information for Cu,[3–7] Ag,[4,7,8] Au,[4,7,9] Al,[6,10,11,19] Pb,[12–14] less complete direct information on Sn,[15–17] Mg,[18] Zn,[20] Cd,[20] and also numerous band structure calculations. Certainly in the noble metals and probably in lithium the Fermi surface deviates markedly from a sphere, but the deviation is a bulge in the direction of the nearest zone faces, as would be expected on a nearly free electron model with a considerable band gap. Indeed for all of the metals listed above, the Fermi surface is recognizably a moderate distortion of the free electron sphere.

The reason for such a resemblance to a free electron band structure does not, of course, lie with the nearly free electron approximation[21]—this approximation requires the atomic potential to be weak compared with the bandwidth, which is certainly not the case. The reason lies instead in the cancellation between the negative potential energy of the electron near an atomic nucleus and the positive kinetic energy associated with the rapid oscillations of the wave function within the

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region of the ion core. Mathematically the oscillations are imposed by the requirement of orthogonality of the valence electron wave functions to all the occupied electron wave functions. In the past, the cancellation has been obvious in the course of calculating matrix elements in the orthogonalized-plane-wave (OPW) method, numerical examples being given for instance in reference 22. Recently, Phillips and Kleinman[23,24] have demonstrated the effect more explicitly by expressing the terms arising from orthogonalization as a pseudopotential[24a] and observing the cancellation in the calculation of the Fourier coefficients. The implication of this cancellation for the justification of the point-ion approximation has been discussed by Phillips.[25]

The purpose of this paper is firstly to demonstrate the cancellation between kinetic and potential energy much more explicitly in real space. Secondly, the theory we develop throws light on the general validity of the various simple valence-electron models mentioned above. Thirdly, it provides a formalism which can treat systems with different numbers of electrons on the same footing, and thus leads to an understanding of the systematic variation of the properties of the elements throughout the periodic table. In Sec. II we start by generalizing the OPW scheme to apply to any valence electron problem including atoms and molecules, and trace its relation to the Phillips-Kleinman (PK) scheme. The demonstration of the cancellation is contained in Sec. III, and in Sec. IV we discuss the relation of the PK scheme to the simple valence-electron models. Section V concludes with a discussion of the systematic trends in the energy levels of monovalent atoms and in the band structures of metals.

II. ORTHOGONALIZED ORBITALS AND THE PK SCHEME

The basis of the OPW method is that the wave function of a conduction electron in a solid is nearly a plane wave, or a linear combination of a few plane waves, in the regions between the ion cores, but that the oscillations of the wave function near the nuclei must be inserted. As first pointed out by Herring,[26] this can be achieved by subtracting some core orbitals from the plane waves, e.g., a $3s-3p$ conduction-electron wave function in sodium is represented by a plane wave with some $1s$, $2s$, and $2p$ functions ϕ_t subtracted:

$$(\mathrm{OPW})=e^{i\mathbf{k}\cdot\mathbf{r}}-\sum_t(\phi_t,e^{i\mathbf{k}\cdot\mathbf{r}})\phi_t \quad (t=1s,\ 2s,\ 2p_x,\ 2p_y,\ 2p_z). \tag{1}$$

This representation works remarkably well because it is a general feature of atomic wave functions that the inner loops of ψ come at about the same radii as the main maxima of the $1s$, $2s$, etc., functions. The coefficients

$$(\phi_t,e^{i\mathbf{k}\cdot\mathbf{r}})=\int\phi_t(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}dv \tag{2}$$

in (1) are chosen to make (OPW) orthogonal to the inner orbitals ϕ_t, and the ϕ_t are chosen[22] as the $1s$, $2s$, etc., eigenfunctions,

$$H\phi_t=E_t\phi_t, \tag{3}$$

of the same Hamiltonian H as we wish to calculate the valence orbitals ψ for, since we know ψ has to be orthogonal to the lower energy solutions of its own wave equation. The expansion of ψ in OPW's with coefficients C_n leads to the secular equation

$$\sum_m[\langle n|H|m\rangle-E\langle n|m\rangle]C_m=0, \tag{4}$$

where $|n\rangle$, $|m\rangle$ represent OPW's with wave vectors $\mathbf{k}_n$, $\mathbf{k}_m$ such that $\mathbf{k}_n-\mathbf{k}_m$ is equal to a reciprocal lattice vector. The cancellation between the potential energy and the kinetic energy which comes from the orthogonalizing terms in (1) can be seen[22] easily in the matrix elements of (4), leading to a nearly free electron band structure with small band gaps and an expansion of ψ in a small number of OPW's.

Clearly, we can apply similar ideas to the calculation of valence orbitals ψ in atoms and molecules, expanding ψ in terms of a few orthogonalized orbitals χ_n

$$\psi=\sum C_n\chi_n, \tag{5}$$

$$\chi_n=f_n-\sum_t(\phi,f_n)\phi_t, \tag{6}$$

where the f_n are some simple set of suitable smooth functions and the ϕ_t, the inner core orbitals again.

Let us now define the function ϕ

$$\phi=\sum_n C_nf_n, \tag{7}$$

which stands in one-to-one correspondence with the true wave function ψ. It represents the smooth part of ψ without the inner oscillations, and from (5) and (6) we have

$$\psi=\phi-\sum_t(\phi_t,\phi)\phi_t. \tag{8}$$

The norm of ϕ is

$$(\phi,\phi)=1+\sum_t|(\phi_t,\phi)|^2, \tag{9}$$

when ψ is normalized to unity. Now as Phillips and Kleinman have shown,[23] the substitution of (8) into the real wave equation,

$$H\psi=E\psi, \tag{10}$$

leads directly to a wave equation for ϕ,

$$(H+V_R)\phi=E\phi, \tag{11}$$

$$V_R\phi=\sum_t(E-E_t)(\phi_t,\phi)\phi_t. \tag{12}$$

The entity V_R is an integral operator or nonlocal

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potential

$$V_Rg(\mathbf{r})=\int V_R(\mathbf{r},\mathbf{r}')g(\mathbf{r}')d^3r', \tag{13}$$

where $g(\mathbf{r})$ is any function and

$$V_R(\mathbf{r},\mathbf{r}')=\sum_t(E-E_t)\phi_t^*(\mathbf{r}')\phi_t(\mathbf{r}). \tag{14}$$

We can separate V_R into

$$V_R=V_{Rs}+V_{Rp}+V_{Rd}+\cdots, \tag{15}$$

with all the inner p orbitals grouped into V_{Rp}, etc. Then (13) and (14) show that only V_{Rp} operates on functions with p symmetry, etc.

In (14), the core energies E_t lie lower than E, so that V_R behaves like a repulsive potential which has the general effect of cancelling some of the negative potential V. Our task now is to express (14) in a form which demonstrates more clearly the details of the cancellation.

III. CANCELLATION OF THE POTENTIAL

One point about the orthogonalized orbital method is that the expansion (5) in terms of orthogonalized orbitals χ_n is actually not unique. If a set of coefficients C_n is a solution of the secular equation for energy E, then so is the set $C_n+\sum_t\alpha_t(f_n,\phi_t)$ a solution for the same energy, where the α_t are arbitrary. The wave function itself is unaffected by the change in the coefficients. The reason for this indeterminacy is that the χ_n are overcomplete. The f_n are complete and independent, but the effect of orthogonalization of the f_n to the core functions is to introduce linear relations among the χ_n.

$$\sum_n(f_n,\phi_t)\chi_n(\mathbf{r})=g_t(\mathbf{r})\equiv 0. \tag{16}$$

Adding any amount of each function $g_t(\mathbf{r})$ thus changes the coefficients of the χ_k as stated without affecting the wave function.

A precisely analogous indeterminacy of ϕ exists in the PK scheme.[27] If one adds

$$\delta\phi=\sum_t\alpha_t\phi_t \tag{17}$$

to ϕ in (8), the addition to the first term is immediately subtracted out by the orthogonalization terms. Alternatively, if ϕ is a solution of Eq. (11) with energy E, then so is $\phi+\sum_t\alpha_t\phi_t$. Thus we are at liberty to impose an additional constraint on ϕ, and this will allow us to simplify (14) through the choice of a particular ϕ. We shall apply the constraint in the form of a variational principle, and there are a number of different quantities one might vary.

In an actual calculation, one would usually expand ϕ in terms of a finite number of functions f_n, $n=1$ to N, and one could then minimize the energy subject to an expansion in this finite function space, giving a unique set of expansion coefficients C_n. Such a procedure in fact leads directly back to the same secular equation (4) as found in the orthogonalized orbitals method. In a sense therefore it does not give anything new, but it is interesting to note in passing what happens to the indeterminacy.[28] Let us consider (4) again as the secular equation for the orthogonalized orbital expansion (5). By taking linear combinations of the χ_n, we can always set up a new set of base vectors to describe our N-dimensional function space. One such base vector (for each t) could be

$$\sum_{n=1}^{N}(f_n,\phi_t)\chi_n(\mathbf{r})=g_t^N(\mathbf{r})\neq 0.$$

If N is large, these functions would have a very small amplitude in view of (16) and their coefficients in the expansion of ϕ would in general be correspondingly large. Thus we can expect large numbers in the solution of (4) which later cancel one another, leading to some numerical difficulties.

A different approach is to choose ϕ to be the smoothest ϕ with the inner oscillations subtracted out as well as possible, i.e., to minimize $\int|\nabla\phi|^2dv/(\phi,\phi)$. The analysis follows closely the one for $V+V_R$ below, and we shall only quote the result. With the particular ϕ mentioned, (12) reduces to

$$(V+V_R)\phi=[V\phi-\sum_t(\phi_t,V\phi)\phi_t]+[(E-\bar{T})\sum_t(\phi_t,\phi)\phi_t]. \tag{18}$$

Here T is the kinetic energy operator, and $\bar{T}$ the expectation value,

$$\bar{T}=(\phi,T\phi)/(\phi,\phi),$$

using the ϕ giving the minimum value.

Alternatively we could demand that the cancellation between V and V_R be as good as possible, i.e., we minimize $|(\phi,\,(V+V_R)\phi)|/(\phi,\phi)$. The variational equation is

$$(\delta\phi,(V+V_R)\phi)-\bar{V}(\delta\phi,\phi)=0, \tag{19}$$

where

$$\bar{V}=(\phi,\,(V+V_R)\phi)/(\phi,\phi) \tag{20}$$

using the minimum ϕ. Substituting the variation (17) gives

$$(\phi_t,\,(V+V_R)\phi)-\bar{V}(\phi_t,\phi)=0. \tag{21}$$

Incidentally, it is not difficult to verify that a ϕ exists which satisfies both (11) and (21): starting with any ϕ that satisfies (11), a set of α_t can be constructed such that (17) satisfies (21), as well as automatically satisfying (11). From (12) we have

$$(\phi_t,V_R\phi)=(E-E_t)(\phi_t,\phi). \tag{22}$$

On subtracting (21) from (22) and substituting back into the right side of (12), we obtain

$$(V+V_R)\phi=[V\phi-\sum_t(\phi_t,V\phi)\phi_t]+[\bar{V}\sum_t(\phi_t,\phi)\phi_t]. \tag{23}$$

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[27] We are grateful to Dr. W. Kohn for emphasizing this point.

[28] We are grateful to Dr. S. F. Boys for emphasizing some of these points; see also V. Heine, thesis, University of Cambridge, 1956.

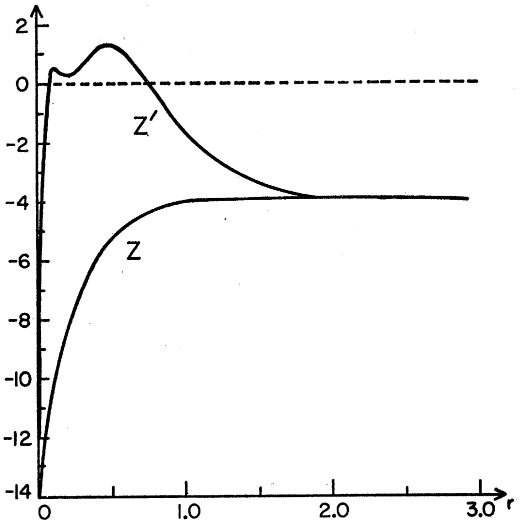

FIG. 1. The cancellation in the potential acting on the valence electron in Si^{3+}: $Z=rV(r)$; $Z'=r[V(r)-(\phi_{1s},V)\phi_{1s}-(\phi_{2s},V)\phi_{2s}]$ $\approx r[V+V_{Rs}]$. $V(r)$ is the same potential[29] as used by Kleinman and Phillips.[24] The σ_{1s}, ϕ_{2s} are from Hartree *et al.*[30] Although the ϕ_t are not eigenfunctions of $V(r)$ as assumed in Eq. (3), this should not affect Z' very much. *Note added in proof.* The repulsive potential in Fig. 1 of reference 24 is twice too large. When corrected, their effective potential is in good agreement with ours. (Private communication from Dr. Kleinman).

In both (18) and (23), we have separated the right side into two brackets. The first bracket has simply the form of a nonlocal potential acting on ϕ, but in the second bracket the coefficient $\bar{V}$ or $(E-\bar{T})$ itself requires a knowledge of ϕ, so that it is not in a useful form for detailed calculations. However, by taking the matrix element with ϕ, we see that the second bracket in each case is smaller than the left side of (18) or (23) by a factor $\sum_t|(\phi_t,\phi)|^2$ which is typically about 0.1. Thus the first bracket represents about 90% of the net potential $V+V_R$ after the cancellation has been done rigorously. For our present semiquantitative discussion, we shall therefore drop the second bracket in (18) and (23). We could take it into account by perturbation theory, in which case its first-order effect is simply to multiply the first bracket by $1+\sum_t|(\phi_t,\phi)|^2$, but in practice, for accurate calculations, one would probably revert to the orthogonalized orbital equation (4).

Retaining only the first bracket of (18) and (23), we have as our net nonlocal potential

$$V+V_R\approx V(\mathbf{r}')[\delta(\mathbf{r},\mathbf{r}')-\textstyle\sum_t\phi_t^*(\mathbf{r}')\phi_t(\mathbf{r})], \qquad (24)$$

where we have assumed V itself is local as in the Hartree approximation. A simple generalization of (24) can be written down if V is nonlocal due to inclusion of exchange terms. Now if the ϕ_t formed an infinite complete set of functions, the square bracket in (24) would vanish identically, giving complete cancellation between V and V_R. In practice we only have a finite number of ϕ_t in the core, but these ϕ_t are quite a good set for representing the bulk of V over the region of the ion core because the 1s, 2s, etc., functions have their main maxima at nicely spaced increasing values of r, so that we get cancellation in (24) to that extent.

We can show the extent of the cancellation in a more perspicuous though slightly approximate form by taking ϕ out of the integral. Suppose ψ and ϕ have the symmetry of a spherical harmonic Y_{lm}. If the cancellation is nearly complete as we suppose it will turn out to be, ϕ varies slowly and inside the ion core can be replaced by Ar^lY_{lm}. The A can then be taken out of the integral, and from (23) we obtain

$$(V+V_{Rl})\phi\approx[V-\textstyle\sum_t(\phi_tr^lY_{lm},V)(\phi_t/r^lY_{lm})]\phi. \qquad (25)$$

We have here reduced $V+V_R$ to a semilocal potential, i.e.; a local potential but different for each l, since in (25) only the ϕ_t having the same l as ϕ contribute. *The extent of the cancellation is the extent to which* $V(\mathbf{r})$ *can be expanded in the finite set of functions* $\phi_tr^lY_{lm}$. Thus the cancellation is almost complete inside the core, but nonexistent outside the core. This is clearly illustrated by the numerical example shown in Fig. 1.

IV. RELATION TO SIMPLE VALENCE-ELECTRON MODELS

In Secs. II and III we have seen how an actual Schrödinger equation $H\psi=E\psi$ may be replaced by $(H+V_R)\phi=E\phi$, where ϕ is essentially the same as ψ but with the rapid oscillations inside the ion core removed. Thus in discussing the valence electrons in atoms, ϕ would be a 1s-like or 2p-like function. In metals ϕ would approximate a plane wave or a simple combination of plane waves; the potential is fairly flat between the atoms and the large negative potential inside the ion core is cancelled off by V_R, so we expect that $V+V_R$ can be treated by perturbation theory. In this way then, we can justify the use of the simple models for treating valence electrons, like the nearly free electron model, which were mentioned in Sec. I, and we obtain a general understanding of why they work as well as they do.

This is satisfactory as far as it goes, but we can develop much more precisely the relationship of our cancellation scheme to any particular model. Let us split $H+V_R$ into a simple model Hamiltonian H_M and a perturbation V_P:

$$H+V_R=H_M+V_P=(p^2/2m+V_M)+(V-V_M+V_R). \qquad (26)$$

For instance, in a metal we might choose $V_M=$ constant; this allows us to absorb the constant part of $E-\bar{T}$ in (18) or of $\bar{V}$ in (23). In an atom or ion a useful V_M might be a cut-off Coulomb potential (see Fig. 1):

$$\begin{aligned} V_M&=Z_c/r, \quad r>r_c,\\ &=0, \quad\quad\;\, r<r_c. \end{aligned} \qquad (27)$$

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We now use the arbitrariness of ϕ (Sec. III), and choose ϕ to minimize

$$(\phi,H_M\phi)/(\phi,\phi);$$

i.e., we choose the ϕ most nearly an eigenfunction of H_M. Analogously to (21), we have

$$(\phi_t,H_M\phi)-E_M(\phi_t,\phi)=0,$$

where E_M is the value of $(\phi,H_M\phi)/(\phi,\phi)$. From (3) we have

$$(\phi_t,H\phi)-E_t(\phi_t,\phi)=0.$$

Subtracting these two equations gives an expression for $E_t(\phi_t,\phi)$, which when substituted into (11) and (12) gives

$$\begin{aligned}(H+V_R)\phi&\\ =H_M\phi&+[(V-V_M)\phi-\textstyle\sum_t(\phi_t,\,(V-V_M)\phi)\phi_t]\\ &+(E-E_M)\textstyle\sum_t(\phi_t,\phi)\phi_t=E\phi.\end{aligned}\tag{28}$$

We shall take the square bracket as our perturbation V_P; if we have chosen V_M to represent V fairly well outside the core, then the cancellation of $V-V_M$ by the V_R should be almost complete, so that V_P is really small. The term following V_P can be neglected completely; alternatively, as remarked in connection with (18) and (23), $(E-E_M)$ in first order is $(\phi,V_P\phi)$ and the expectation value of the whole term is

$$(\phi,V_P\phi)\textstyle\sum_t|(\phi_t,\phi)|^2\approx 0.1(\phi,V_P\phi),$$

so that it can be taken into account correctly to first order by multiplying V_P by $1+\sum_t|(\phi_t,\phi)|^2\approx 1.1$ in a typical case.

A criterion which can be used to test whether $V_P\phi$ may be regarded as small compared with $(\Delta E)\phi$, where ΔE is of the magnitude of a typical separation between valence-electron energy levels, is suggested by the standard criterion for convergence of generalized Fourier series:

$$G=[(g,g)-\textstyle\sum_t|(\phi_t,g)|^2]/(\Delta E)^2(\phi,\phi)\ll 1,\tag{29}$$

where

$$g=(V-V_M)\phi.\tag{30}$$

Whenever the criterion (29) is well satisfied, ϕ is close to f, an eigenfunction of the model Hamiltonian H_M. It is sufficient, therefore, to require that

$$G'=[(g',g')-\textstyle\sum_t|(\phi_t,g')|^2]/(\Delta E)^2(f,f)\ll 1,\tag{29$'$}$$

where

$$g'=(V-V_M)f.\tag{30$'$}$$

Thus a knowledge of the solution of the real problem ϕ is not required to test the accuracy of the model. If V_M contains adjustable parameters, these can be chosen in such a way as to minimize G', which is the same as requiring optimum cancellation of the difference between V and V_M by the orthogonalization terms. It is interesting to note that in this variational principle the model Hamiltonian itself is varied to approximate closely to the actual Hamiltonian $H+V_R$; it contrasts with the usual uses of model Hamiltonians, when the parameters of the model are varied to minimize the expectation value of the true Hamiltonian with the model wave function.

TABLE I. Energy levels of alkali atoms.[a]

	$-\epsilon_s$ (ev)	$-\epsilon_p$ (ev)	$\epsilon_s-\epsilon_p$ (ev)	r_a (10^{-8} cm)
H	($1s$) -13.60	...	...	...
Li	($2s$) -5.39	($2p$) -3.54	1.85	1.72
Na	($3s$) -5.14	($3p$) -3.04	2.10	2.10
K	($4s$) -4.34	($4p$) -2.73	1.61	2.61
Rb	($5s$) -4.18	($5p$) -2.60	1.58	2.81
Cs	($6s$) -3.89	($6p$) -2.45	1.44	3.04

[a] $-\epsilon_s$ and $-\epsilon_p$ are the energies of the levels relative to the ionized state of the atom. ϵ_p represents the average for the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ levels. Values of ϵ_s, ϵ_p are taken from reference 31, values of the atomic radius r_a from reference 21.

V. ATOMIC ENERGY LEVELS

Consider the ground states of the alkali atoms (Table I). By using the cancellation theorem and Eq. (11), we always reduce the wave function of the valence electron to a $1s$-like function. We have therefore a basis for comparing the different alkali atoms, and the energy levels just depend on the goodness of the cancellation. The first thing we note is that in the s series, the first level H $1s$ has a very low energy compared with Li $2s$, Na $3s$, etc.; this is because in the case of H $1s$ there are no lower core orbitals to do any cancelling. The same effect can be seen in the Li $2p$ level, though to a much lesser extent because here the centrifugal $l(l+1)/r^2$ term in the radial wave equation to some extent makes up for the lack of a $1p$ function. After that, Table I shows that the levels in both the s and p series get progressively more weakly bound: On the one hand, the number of functions increases approximately as the square root of Z so that the cancellation gets better and better; on the other hand, the potential itself gets deeper rather less rapidly than proportional to Z. The facts show that the first tendency dominates over the second, as is hardly surprising since from (25) the net potential left in the region of the core after cancellation is the remainder after expanding $V(r)$ in the series of n functions, and due to the rounded shape of the functions we might expect the series to converge at least as fast as $1/n^2$, i.e., as $1/Z$. These remarks are at present, of course, no more than qualitative comments, but they show how Eqs. (25) and (28) open the way for a quantitative comparison between different atoms.

Incidentally, we note from Fig. 1 that the potential is not cancelled off for $r<r_K$, the radius of the K shell. For functions of s-like symmetry, (25) reduces to

$$V+V_R=V-\sum_{\nu=1}^{n}(\phi_{\nu s},V)\phi_{\nu s}\tag{31}$$

where n is the principal quantum number of the outermost s electron in the core. Now $\phi_{\nu s}(r) \rightarrow$ const and $V(r) \rightarrow -\infty$ as $r \rightarrow 0$, so that $V+V_R$ contains an uncancelled spike $-Ze^2/r$ of radius r_K. Now r_K is approximately a_0/Z, where a_0 is the Bohr radius, so that in first-order perturbation on ϕ the spike contributes an energy of about $4\pi|\phi(0)|^2 Z r_K{}^2 \sim 1/Z$ rydbergs which is unimportant for large Z.

Table I also shows how the radii r_a of the alkali atoms increase significantly with Z. Part of this is due to the decreasing ϵ_s since $\phi_{1s} \sim \exp[-(\epsilon_s)^{\frac{1}{2}} r]$ at large r, giving $r_a \propto \epsilon_s{}^{-\frac{1}{2}}$. However, the observed increase in r_a is considerably greater than this, and must be due to the fact that good cancellation inside the core pushes ϕ out to the regions of negative potential energy outside the core.

We turn now to the other monovalent series, the noble metals. Their ϵ_s ionization energies are rather larger than those of the alkalis:

$$\text{Ag, 7.57 ev;} \quad \text{Cu, 7.72 ev;} \quad \text{Au, 9.22 ev.} \qquad (32)$$

The reason for this is as follows. In copper, for example, the $3d$ shell is rather loosely bound compared with the cores of the alkali atoms, and consequently extends out to a considerably larger radius than the $3s$ function. Thus the $3s$ function in (31) is incapable of cancelling off the potential in the outer regions of the core, leaving a large negative potential which produces a tightly bound $4s$ level, i.e., a large ϵ_s. Thus the looser the d shell, the tighter the next s shell is; and if we take the order of increasing looseness of the d shells as Ag, Cu, Au as evidenced by their color and chemical valencies, we note that this is indeed the same as their order of increasing ϵ_s in (32).

A rough theory has already been given in reference 1 relating the electronic band structures of the alkali metals to the atomic parameters $\epsilon_s - \epsilon_p$ and r_a, and the argument seems to be applicable qualitatively also to groups IIA and IIIA of the periodic table. In Na, Mg, Al, the band gaps appear to be very small.[31] As Z increases, ϵ_s ($\propto r_a{}^{-2}$) decreases more rapidly than $\epsilon_s - \epsilon_p$, resulting in an increasing band gap with the s-like state at the gap being the lower one. In Li and Be, however, there are large band gaps with the p-like state lowest, due to the small r_a and the abnormally low $\epsilon_s - \epsilon_p$ which we have seen is in turn due to the absence of a $1p$ shell. As Ziman[31] has pointed out, these systematic trends in the band structures are directly reflected in the electrical resistivities and Hall coefficients[32] of these metals as well as in other properties.

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[31] F. Ham, J. M. Ziman, and other contributors, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

[32] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 488.

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Configuration Interaction in Simple Atomic Systems*†

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The ground-state wave functions of the helium, lithium, and beryllium atoms were approximated by a superposition of configurations with expansion lengths ranging from 35 for helium to 55 for beryllium. The discrepancies in the total energy are 0.014 ev for helium, 0.026 ev for lithium, and 0.17 ev for beryllium. A 19-configuration function was also applied to the lowest ${}^3S$ state of helium, with a resulting accuracy of 0.0005 ev. The calculations were also made on all the isoelectronic series of ions through $Z=8$, the discrepancy remaining of the same order of magnitude but increasing with increasing Z. A lower bound to the electron affinity of lithium is set at 0.4773 ev, with the most probable value, obtained by extrapolating the isoelectronic series, being placed at 0.62 ev.

INTRODUCTION

PROBABLY the most widely used and most generally successful approach to many-particle quantum mechanics is the independent-particle model, which at its best is represented by the Hartree-Fock approximation.[1] Physically, this approximation amounts to treating the interparticle interactions in only an average fashion, i.e., each particle is assumed to move in only the average field of all the other particles of the system. Mathematically, the method consists of approximating the state function as an antisymmetrized product of one-particle functions (spin orbitals). Subjecting such a function to the variational principle leads to the well-

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[1] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).