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Multi-Ion Interactions and Structures in Simple Metals*

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The total energy of simple metals is calculated formally to all orders in the pseudopotential. The leading term (in the pseudopotential expansion) of the n-ion interaction is obtained from the nth-order terms and the asymptotic form for large separations is evaluated explicitly. The resulting n-ion interaction is proportional to $(E_F/k_F)(\lambda/k_F)^n[\cos k_F(l_1+l_2+\cdots+l_n)]/l_1 l_2\cdots l_n(l_1+l_2+\cdots+l_n)$, where the l_i are consecutive segments of a straight-line path connecting the n ions and λ is of the order of a pseudopotential form factor divided by the Fermi energy. This is to be summed over all continuous paths connecting the n ions. The familiar two-body interaction proportional to $(\cos 2k_F r)/r^3$ is a special case. The three-body interaction is found to be strongest when the three ions form a straight line and are separated by nearest-neighbor distances. The assumption that the influence of d-state hybridization upon this interaction dominates the determination of structures leads to the correct distribution of cubic and hexagonal structures among the monovalent and divalent metals and to appropriate high and low axial ratios among the hexagonal structures.

I. INTRODUCTION

The essence of pseudopotential theory,[1] as applied to simple metals, is a treatment of the interaction between electrons and ions as a perturbation. It is assumed at the outset that the complete solution of the electron-ion problem, within a self-consistent-field approximation, would yield a good description of the metal. The only important approximation made in the solution of that one-electron problem is the perturbation expansion, ordinarily carried to second order. This approach gives us not only a mathematical basis for treating the entire range of metallic properties, but also a conceptual basis for thinking about these systems.

An important conceptual feature of the theory is that the second-order energy can be written as a two-body central-force interaction between atoms. This is plausible physically since the terms in second-order perturbation theory may be thought of as two consecutive scattering events by a single electron; they can therefore involve only two atoms. The inclusion of third-order perturbation theory will introduce explicit three-body interactions, etc. A second important feature of the second-order theory is the form of the two-body interaction. The asymptotic form for large distances is readily calculated and is proportional to $(\cos 2k_F r)/r^3$, exhibiting the familiar Friedel oscillations. Furthermore, this asymptotic form remains qualitatively correct even to distances as small as the interatomic distance in the metal, as seen in Fig. 1.

In the present study we will carry these calculations to higher order in the pseudopotential and obtain the asymptotic form of the leading term in the multi-ion interactions. It is important to be clear about what is being included and what is not being included in this analysis. We are *not* systematically including all higher-order terms in the calculation of the total energy. In particular, such a complete calculation would require the self-consistent recalculation of the pseudopotential itself in each order; the configuration of an ion's neighbors would affect the pseudopotential on that ion. We will neglect this effect and in all orders write the pseudopotential as the superposition of identical ionic pseudopotentials centered on the ion nuclei, and in any applications will use the individual pseudopotential calculated self-consistently to first order. Secondly, in each order we will focus upon the multi-ion interaction which first occurs in that order. Thus in third order we will obtain the three-ion interaction but will not compute the additional two-body interaction which arises in third

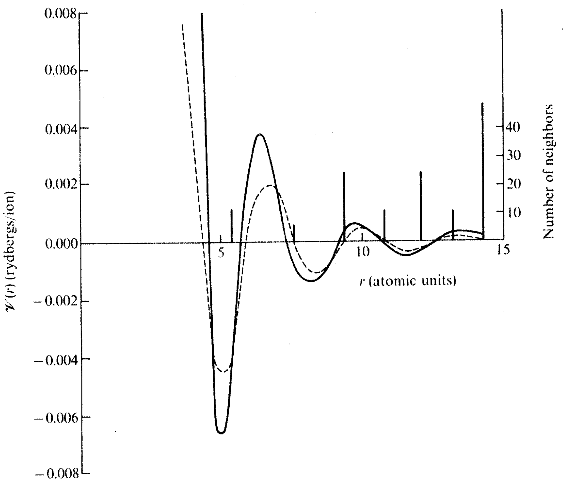

FIG. 1. Two-body interaction between ions for aluminum. The dashed line is the asymptotic form. Also shown is the distribution of neighbors as a function of distance for the fcc structure.

order. Such neglected terms may be thought of as arising from, for example, the scattering of an electron by one atom, then by second, and again by the first. Such contributions will, like the second-order terms, give a two-body central force but will be smaller than the second-order interaction. For reasons to be discussed in Sec. III these contributions may not, however, be negligible.

In some sense the terms which we *do* include are the most interesting. In seeking, for example, the features which determine the crystal structure it is noted that the zero-order and first-order terms in the pseudopotential are independent of the configuration of the ions (although they do depend upon the total volume). Thus the two-body interaction which arises in second order is the leading term which influences the crystal structure. The second-order terms which are independent of configuration are of very much less interest. When we compare the energies of structures using this two-body interaction we find in fact that these contributions are quite insensitive to structure, because of their two-body central-force nature. In going to third order we obtain three-body forces which depend explicitly upon the angles between interionic separations, and we hope there to find an understanding of crystal structures. It would not be so interesting to examine the modification of the *two*-body interaction which arises in third order. It also seems likely that the explicit multi-ion interactions which would arise in a higher-order self-consistent recalculation of the pseudopotential would be less important than the direct terms we calculate. This speculation is based partly on the fact that in the second order the screening of the pseudopotential plays only a minor role.

The calculation of the total energy to third order is a very intricate task. It appears to have first been accomplished by Lloyd and Sholl[2] and independently by Brovman, Kagan, and Holas,[3] both making a local approximation to the pseudopotential. The result is given as a function of two wavenumbers which may be written in closed form. The third-order energy is to be obtained by a double sum of this function over the wave-number lattice. The function is the third-order counterpart of the second-order energy-wave-number characteristic. Brovman *et al.* have included these terms in a calculation of the vibration spectrum of magnesium and have found their effects to be appreciable. In the author's unpublished calculations, the third-order contribution to the energy was found to be typically one-quarter as large as the second-order contribution. In comparing the energies of crystal structures we have found the third-order terms to vary from structure to structure by an amount comparable to the second-order terms, but we did not find their inclusion improved the prediction of structures. In addition, we found that after performing the first sum over the wave-number lattice, the remaining function to be summed over the wave-number lattice was quite insensitive to structure and therefore a large portion of the third-order energy was in fact describable in terms of a two-body interaction. By isolating a three-body interaction in the present analysis we hope to focus more sharply on the novel aspects of the third-order and higher-order terms.

The obtaining of the asymptotic form of the multi-ion interactions is a very much simpler problem than the calculation of the full interaction, and in fact we will be able to obtain these forms analytically. In addition, we find that the asymptotic forms are very simple and intuitively understandable. Thus conceptually they are of much more value than complete interactions which would necessarily need to be tabulated or plotted over a multidimensional array. In fact, we obtain universal forms which may be applied to any metal by substitution of the appropriate pseudopotential form factors for that metal. Another feature of the asymptotic calculation is that it becomes unnecessary to make a local approximation to the pseudopotential. Finally, we may hope that these asymptotic forms, which we believe are rigorous at large interionic distances, may remain qualitatively valid even at short distances, as was the case of the two-body interaction.

The procedure for obtaining asymptotic forms is analogous to that used in the second-order term.[4] The matrix elements in the perturbation theory are factored into structure factors and form factors, and terms involving a specific set of ions are isolated. The sums over wave number are converted to integrals, and the singularities, which ultimately arise from the energy denominators, dominate the behavior at large distances. It is possible to take the third-order results[2,3] and proceed much as in the second-order case to obtain the asymptotic form. It is, however, much simpler and much more general to return to the perturbation expression itself. Because the analytic behavior at the singularities is essential and because we wish to proceed to high order, this is most conveniently done in the context of the one-electron Green's function. We proceed to that calculation.

II. CALCULATION OF ASYMPTOTIC FORM

Within the one-electron approximation the system is completely describable by a one-electron Green's function $G_\pm(\vec{r}, \vec{r}\,'; t, t')$.[5] In the context of the pseudopotential formulation, this should be regarded as a pseudo-Green's-function, but the distinction is inessential in the calculation of the total energy. After Fourier transforming in time and space we may sum the diagonal terms to obtain the number of states per unit energy:

$$N(E)=\frac{2}{2\pi i}\sum_{\vec{k}}\,[G_+(\vec{k},E)-G_-(\vec{k},E)]\;. \tag{1}$$

The factor of 2 is for spin degeneracy. The Green's function itself is expanded in a perturbation series in the pseudopotential,

$$G_\pm(\vec{k},E)=\sum_n G^n_\pm(\vec{k},E)\;. \tag{2}$$

In zero order we have the free-electron Green's function,

$$G^0_\pm(\vec{k},E)=\frac{1}{E-\epsilon_{\vec{k}}\mp i\epsilon}\quad, \tag{3}$$

where $\epsilon_{\vec{k}}$ is a free-electron energy and ϵ is a real positive small number. The nth-order term may also be written down and summed over wave number since it is that sum which enters the density of states in Eq. (1).

Then we have

$$\sum_{\vec{k}_1} G^n_\pm(\vec{k}_1,E)=\sum_{\vec{k}_1\vec{k}_2\cdots\vec{k}_n}\frac{\langle\vec{k}_1|W|\vec{k}_n\rangle\langle\vec{k}_n|W|\vec{k}_{n-1}\rangle\cdots\langle\vec{k}_2|W|\vec{k}_1\rangle}{(E-\epsilon_1\mp i\epsilon)(E-\epsilon_2\mp i\epsilon)\cdots(E-\epsilon_n\mp i\epsilon)(E-\epsilon_1\mp i\epsilon)}\;. \tag{4}$$

Note that the energy denominator with the energy ϵ_1 of the state $|\vec{k}_1\rangle$ appears twice, but since all wave numbers are summed a rotation of indices does not affect the results. Then, noting that the energy E appears only in the denominators (the pseudopotential operator need not explicitly depend on energy), we see that Eq. (4) may be rewritten

$$\frac{2}{2\pi i}\sum_{\vec{k}_1} G^n_\pm(\vec{k}_1,E)=-\frac{d}{dE}\,g^n_\pm(E)\quad, \tag{5}$$

where

$$g^n_\pm(E)=\frac{1}{n\pi i}\sum_{\vec{k}_1\vec{k}_2\cdots\vec{k}_n}\;\prod_{j=1,\ldots,n}\frac{\langle\vec{k}_{j+1}|W|\vec{k}_j\rangle}{E-\epsilon_j\mp i\epsilon}\;. \tag{6}$$

We take cyclic indices such that the state $j=n+1$ is the state $j=1$.

At this point we may factor each matrix element into a form factor (the matrix element of an individual ionic pseudopotential) and a structure factor,

$$\langle\vec{k}_{j+1}|W|\vec{k}_j\rangle=\langle\vec{k}_{j+1}|w|\vec{k}_j\rangle\left(\frac{1}{N}\right)\sum_t e^{-i(\vec{k}_{j+1}-\vec{k}_j)\cdot\vec{r}_t}\;, \tag{7}$$

where the sum is over the positions $\vec{r}_t$ of all N ions. This form may be substituted in Eq. (6) and the sum over atomic positions taken outside. g^n then becomes an n-fold sum over all ion positions. In each term we write the $\vec{r}_t$ which appears in the $\vec{k}_{j+1}-\vec{k}_j$ structure factor as $\vec{r}_j$. In the product of structure factors each $\vec{k}_j$ appears twice and the product over structure factors in that term becomes

$$\frac{1}{N^n}\prod_j e^{i\vec{k}_j\cdot(\vec{r}_j-\vec{r}_{j-1})}\quad.$$

For a particular collection of n atoms we define a path $\vec{l}_j=\vec{r}_j-\vec{r}_{j-1}$ among those atoms. Then each term in Eq. (6) may be rewritten

$$\delta g^n_\pm(E)=\frac{1}{n\pi i N^n}\sum_{\vec{k}_1,\vec{k}_2\cdots\vec{k}_n}\;\prod_j\frac{\langle\vec{k}_{j+1}|w|\vec{k}_j\rangle\,e^{i\vec{k}_j\cdot\vec{l}_j}}{E-\epsilon_j\mp i\epsilon}\quad, \tag{8}$$

and this is ultimately to be summed over every path connecting n ions. We will in fact include only paths in which all n ions are different, since only these give n-ion interactions.

We now have a series of identical summations over the wave numbers $\vec{k}_j$. These are replaced by integrations, taking spherical coordinates with axis along $\vec{l}_j$:

$$\sum_{k_j}\frac{\Omega}{(2\pi)^3}\int_0^\infty dk_j\,k_j^2\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi}d\varphi\;.$$

As we vary the angle of a particular $\vec{k}_j$ there are two form factors which vary,

$$w_j\equiv\langle\vec{k}_{j+1}|w|\vec{k}_j\rangle\;,\qquad w_{j-1}\equiv\langle\vec{k}_j|w|\vec{k}_{j-1}\rangle\;,$$

as well as the exponential $e^{i\vec{k}_j\cdot\vec{l}_j}$. However, when l_j is very large the exponential oscillates rapidly and the only appreciable contributions arise at the points of stationary phase, when $\theta = 0$ and $\theta = \pi$. Thus the summation becomes[6]

$$\sum_{\vec{k}_j} \rightarrow w_j w_{j-1} e^{i\vec{k}_j\cdot\vec{l}_j} \frac{\Omega}{(2\pi)^2}\int_0^\infty dk_j\, k_j^2 [w_j(+)\, w_{j-1}(+)\, e^{ik_j l_j} - w_j(-)\, w_{j-1}(-)\, e^{-ik_j l_j}]/ik_j l_j \;. \quad (9)$$

Here $w_j(+)$ is the form factor evaluated with $\vec{k}_j$ parallel to $\vec{l}_j$ and $w_j(-)$ is evaluated with $\vec{k}_j$ antiparallel to $\vec{l}_j$. In the first term we change variables to $k = k_j$ and in the second to $k = -k_j$. They may be combined to give

$$\sum_{k_i} \frac{w_j w_{j-1} e^{ik_j l_j}}{E - \epsilon_j \mp i\epsilon} = \frac{\Omega}{(2\pi)^2 i l_j}\int_{-\infty}^{\infty} \frac{dk\, k\, w_j w_{j-1} e^{ikl_j}}{E - k^2 \mp i\epsilon} \;. \quad (10)$$

We have reinserted the energy denominator, which was constant in the angular integrations, and we evaluate form factors in accordance with the sign of k. We have also replaced the free-electron energy ϵ_j by the kinetic energy k_j^2 (in rydbergs if k_j is in atomic units). The remaining integral may be evaluated by closing a contour in the upper half-plane. The interesting region is with E positive. We write $\kappa = \sqrt{E}$. In the integrand with $-i\epsilon$ in the denominator there is a pole above the real axis near $k = -\kappa$. In the integrand with $+i\epsilon$ in the denominator the pole above the real axis occurs near $k = \kappa$. The form factors (which are screened) have no poles on the real axis, and any pole away from the axis would contribute only exponential terms to the ion-ion interaction. Thus for obtaining the asymptotic form of the interaction each integral of the form appearing in Eq. (10) is equal to the contribution of a single pole. The result, when substituted in Eq. (8), is

$$\delta g_\pm^n(\kappa^2) = \frac{1}{i\pi n}\left(\frac{-\Omega}{4\pi N}\right)^n \prod_j \frac{w_j(\mp)\, e^{\mp i\kappa l_j}}{l_j} \;. \quad (11)$$

It is convenient to define the distance around the path $s = \sum l_j$ and to note that the same pseudopotential form factors enter when all wave numbers are reversed. We can then combine the plus and the minus terms:

$$\delta g^n = \delta g_+^n - \delta g_-^n = \frac{-2}{n\pi}\left(\frac{-\Omega}{4\pi N}\right)^n \sin\kappa s \prod_j \frac{w_j}{l_j} \;. \quad (12)$$

This is to be summed over all paths connecting n ions and then summed over all orders to give a total g. The density of states, according to Eqs. (1), (2), (5), and (12), is given by

$$N(E) = -\frac{d}{dE}\, g(E) \;. \quad (13)$$

The total energy is obtained by integrating $EN(E)$ from zero to the Fermi energy μ:

$$E_{\text{tot}} = \int_0^\mu \left(\frac{-dg}{dE}\right) E\, dE = -g(E)E\,\Big|_0^\mu + \int_0^\mu g(E)\, dE \;. \quad (14)$$

We wish to obtain the change in this total energy as the positions of the atoms are changed.

Let us now imagine an infinitesimal change in ion positions giving an infinitesimal change in g. There must then be a change in the Fermi energy $d\mu$ such that the total number of electrons [seen from Eq. (13) to be $-g(\mu)$] is not changed. Thus, the change in the surface term in Eq. (14) is $-g(\mu)\,d\mu$, just cancelling the effect of changing the upper limit in the integrals. We conclude that forces on the ions, and therefore the interionic potentials, are computed at fixed Fermi energy. As is familiar in the two-ion case, the potentials are volume dependent, but this causes no difficulty if properties are computed at constant volume.

The remaining integral of Eq. (14) contains contributions from each order. In each order we must add the contributions from each path among the appropriate number of ions, using Eq. (12). Thus the interaction between a given set of n ions is simply the integral over Eq. (12),

$$\int_0^{k^2} \delta g^n(\kappa^2)\, d(\kappa^2) = \frac{4k}{n\pi}\left(\frac{-\Omega}{4\pi N}\right)^n \left(\frac{\cos ks}{s}\right) \prod_j \frac{w_j}{l_j} \;, \quad (15)$$

summed over all continuous paths among those ions. k is the Fermi wave number. [Note that a term dropping more rapidly with s was discarded in obtaining Eq. (15); that is, only the first term of $\cos ks - (\sin ks/ks)$ was kept.]

There are $n!$ such paths, but for a given continuous path shape the result is independent of which ion is numbered one, and is independent of the direction in which the path is traversed. Thus we may multiply Eq. (15) by n and sum over path shapes and path directions, the latter giving a factor of 2 in all cases but $n = 2$. (For $n = 2$ it gives a factor of 1.) Thus we may write the asymptotic form of the n-body interaction

$$\mathcal{V}(r_1, \ldots, r_n) = \frac{4E_F}{\pi}\left(\frac{-3\pi Z}{4E_F k}\right)^n \times \sum_{\substack{\text{path and}\\ \text{direction}}} \frac{w_1 w_2 \cdots w_n}{l_1 l_2 \cdots l_n}\left(\frac{\cos k\,(l_1 + \cdots l_n)}{k(l_1 + \cdots l_n)}\right) \;. \quad (16)$$

We have eliminated the volume of the system by writing

$$\frac{2\Omega}{(2\pi)^3}\left(\frac{4}{3}\right)\pi k^3 = NZ \;,$$

where Z is the number of electrons per ion, the valence. This is our principal result. Note that in this notation the contribution of the n-body

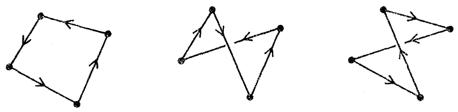

FIG. 2. Three paths which must be summed to obtain the four-ion interaction.

forces to the total energy is given by

$$E^n_{\text{tot}} = \frac{1}{n!} \sum_{r_1, \ldots, r_n} \mathcal{V}(r_1, \ldots, r_n) ,$$

where the $n!$ compensates for the same collection of ions appearing in $n!$ different permutations.

Physically we may think of each term as arising from an electron with the Fermi energy scattering successively from each of the ions, making straight-line trajectories between scattering events. The resulting interaction decreases with each path length and with the total path length and oscillates with the phase integral around the path. Correspondingly, each form factor is determined by computing the wave-number transfer in each of these scattering events.

The two-body interaction is obtained by setting $n=2$. There is one direction and one path and l_1 equals l_2. Thus the two-body interaction is given by

$$\mathcal{V}(r_1, r_2) = \frac{9\pi Z^2 w^2}{8E_F} \left(\frac{\cos 2kl}{(kl)^3}\right) , \tag{17}$$

in agreement with earlier results.[4]

In computing the three-body interaction the sum over the direction gives a factor of 2, and there is a single path, the triangle connecting the three ions. In the four-body interaction there are again two directions and three path shapes, the square and two bowties shown in Fig. 2. In the five-body interaction there are 12 path shapes consisting of five birds, five fish, a pentagon, and a star.

III. INFLUENCE ON STRUCTURES

We will discuss the role of the many-ion interactions in the context of the determination of crystal structures. The tendencies caused by the three-ion interaction in particular are most suggestive.

We note first that the three-ion interactions tend to be weaker than the two-ion interactions by a factor of the pseudopotential form factor divided by the Fermi energy, typically one-tenth. However, we may note also that, when the three ions in question lie very nearly on a straight line, one of the pseudopotential form factors which enters is that for forwardscattering equal to $-\frac{2}{3}E_F$; in this case the three-body interaction cannot be considered as small in comparison to two-body interactions. The fact that third-order terms become comparable to second-order terms when small-angle scattering is involved has been emphasized particularly by Brovman.[7]

We will focus upon this effect and, since the three-ion interaction drops very rapidly with distance (with the fourth power of the interatomic separation), we will focus particularly upon linear arrangements of three ions in which two of the separations are the nearest-neighbor distance. The three-ion interaction (and in particular, the asymptotic form) can tend to favor, or can tend to prevent, the linear arrangement, depending upon the ratio of the separation to the Fermi wavelength. We consider the interaction of Eq. (16) with $n=3$ and with the three ions nearly aligned. An electron following a path among these three will make two back scatterings and one forward scattering. Thus one pseudopotential form factor is $-\frac{2}{3}E_F$ and two are backscattering form factors, the same as those which enter the second-order interaction; we write these simply as w and neglect their variation with deflection of the ions. We write the angular deviation from a straight line as θ (see Fig. 3) and evaluate Eq. (16) for small θ. The result is

$$\mathcal{V} = \frac{9\pi Z^2 w^2}{E_F(4kd)^3} \left[\left(\frac{2\pi Z}{kd}\right)\cos 4kd + \left(\frac{\pi Z}{kd}\right)(3\cos 4kd + 4kd \sin 4kd)\,\frac{\theta^2}{8}\right] .$$

Note that by writing the forward scattering form factor explicitly we have obtained this third-order term in a form very similar to a second-order

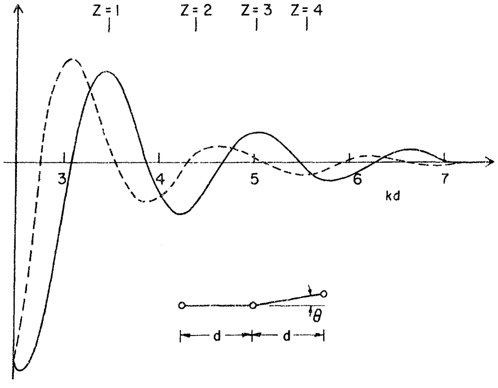

FIG. 3. Curves for the asymptotic form of the three-body interaction between ions, with the configuration shown below, as a function of kd, with k the Fermi wave number and d equal to the nearest-neighbor distance in close-packed structures. The dashed curve is proportional to the interaction energy with $\theta=0$. The solid curve is proportional to the second derivative of this energy with respect to θ at $\theta=0$. The values of kd corresponding to valence Z are shown.

term. In fact, the second-order coupling between the end atoms is of almost identical form. It may be evaluated from Eq. (17). In the result the θ-independent term is the same as the first term in Eq. (18), but without the factor $2\pi Z/kd$. The more interesting θ-dependent term is the same as the final term in Eq. (18), without the factor $\pi Z/kd$. We may think of the coefficient of the θ^2 term as a spring constant favoring (or opposing when negative) alignment of the three ions. The third-order contribution to the spring constant is $\pi Z/kd$ times as large as the second-order term. This is a factor of 0.90, 1.44, and 1.88 for valence one, two, and three, respectively, and for d equal to the nearest-neighbor distance in close-packed structures. With respect to the tendency to align these ions the third-order term is of approximately the same importance as the second-order term.

These particular interactions are also very relevant to the determination of structures. It is well known that both face-centered-cubic (fcc) and hexagonal-close-packed (hcp) structures can be obtained by the stacking of close-packed planes. The nearest-neighbor distance and the number of nearest neighbors are identical in the two structures. The difference comes, as we stack each plane, in whether we do it such that each ion will form a straight line with ions in the prior two planes (face centered cubic) or such that it does not (hexagonal close packed). Thus if the energy is minimum when the three ions are aligned, the corresponding contributions to the energy may be thought of as favoring the cubic structure; if it is a maximum, we may think of it as favoring a hexagonal, or other noncubic, structure. It is important that we consider the angle-dependent term rather than the constant term of Eq. (18), as it is the comparison of the energies in different structures which is relevant. The second qualitative feature which is of some interest is whether the third-order energy for three aligned ions increases or decreases with an increase in the spacing. This can be of interest in the hexagonal structure, where the aligned ions lie only in the basal plane and the dependence upon spacing can cause a change in axial ratio. It will not be of interest in the cubic structures, where it only contributes another volume dependence.

We note that the interactions represented by Eq. (18) depend (except for a positive scale factor) only upon kd, which in turn depends only upon the valence. In addition, the ratio of these interactions to their second-order counterparts depends only upon valence. We may see what the effects of the interactions are by plotting the first and second terms of Eq. (18) as a function of kd, again with d equal to the nearest-neighbor distance in close-packed structures. The result is shown in Fig. 3. A positive value for the solid line implies an energy minimum with linear alignment. Thus we see that cubic structures are favored for valence one and three, hexagonal structures for valence two. We have noted that the tendency toward linear alignment (for $Z = 1$ or 2) is the same if body-centered-cubic (bcc) nearest-neighbor distances are used with Fig. 3 rather than close-packed distances, and therefore we do not distinguish the two cubic structures. A negative slope of the dashed line would suggest the tendency for close-packed lines to lengthen; a positive slope, the tendency for them to shorten. Figure 3 suggests a tendency for any hexagonal monovalent or trivalent metals to have low axial ratios and any divalent metals to have high axial ratios. These tendencies correlate with experiment about as well as could any tendencies which depended upon valence alone. However, to be convincing any correlation must include the trends with row as well as with column in the Periodic Table, particularly with the monovalent and divalent metals where clear trends are evident.

We begin with sodium, magnesium, and aluminum, for which the earliest[8] second-order calculations (as well as most subsequent calculations) correctly gave hcp, hcp, and fcc, respectively. For sodium the third-order terms would suggest a tendency toward cubic and, in fact, the second-order calculation[8] overestimated the bcc-hcp energy difference by a factor of 30. The third-order terms have contributed in the right direction without changing the stable structure. In magnesium and aluminum the third-order terms favor the same structures as did the second-order terms. If the third-order terms have increased the axial ratio in magnesium, it is by a very small amount. We will not concern ourselves with the lighter lithium and beryllium, for which the pseudopotential expansion has ordinarily proved unreliable, but for which the structures are in fact the same as sodium and magnesium.

What differences might we expect for the heavier monovalent and divalent metals? The feature which distinguishes each of these metals from sodium and magnesium is that each lies either at the end or the beginning of a transition-metal series. In terms of electronic structure this means that in the alkalis and the alkaline earths there is a d resonance just above the Fermi energy; in the noble metals and in zinc and cadmium there is a d resonance below. The effect of these resonances may be included within the framework of pseudopotential theory as hybridization contributions to the transition-metal pseudopotential.[9] When the resonance lies below the Fermi energy this hybridization will always have the effect of adding a positive term to the backscattering form factor without changing the forward scattering form factor. In a similar way Moriarty has found[10] that a resonance above will always add a negative term to the backscattering form factor without affecting the forward scattering one. To see what effect this would have on structure determination would require extensive calculation of both second-order and third-order terms. In particular, though we argued that we have isolated the dominant contributions of the third-order term, the second-order term involving second neighbors that we have isolated is most certainly not dominant among the second-order terms. The best we can do is to look just at the effect these hybridization contributions have on the third-order interaction and not guess their effect on the total second-order energy.

In the heavy alkali metals the backscattering form factor is negative[11] (it is near zero in potassium) and the hybridization makes them even more negative, increasing the trend to cubic structures. Though without hybridization the third-order effect was almost strong enough to make sodium cubic, with hybridization it wins out in all of the heavy alkalis, which are found to be bcc. In the noble metals the pseudopotential form factor for backscattering is positive and is increased further by hybridization enhancing the tendency to be cubic; in this case they are found to be fcc. The differences in energy between these two cubic structures depend very much on nearest-neighbor interactions and in particular upon the second-order terms which are out of the context of our discussion.

In the alkaline earths the pseudopotential form factor for backscattering is positive and is reduced by hybridization with the d resonance above (Moriarty[10] in fact finds that it reverses the sign of the total form factor). Thus the tendency toward hexagonal structures is reduced by hybridization; cubic structures are favored. Calcium and strontium are, in fact, fcc and barium is bcc. In zinc and cadmium, in contrast, hybridization with the d bands below enhances the form factor, thereby enhancing the tendency to hexagonal structures. Furthermore, it enhances the tendency to high axial ratios; both zinc and cadmium are, in fact, found to have high axial ratios, in contrast to magnesium, beryllium, and the light alkalis. We have omitted from consideration mercury, which has a complex structure, and the trivalent metals, which show no systematic trends experimentally nor for which are hybridization effects expected to be appreciable.

IV. DISCUSSION

It is indeed dangerous to isolate a single term in the total energy and correlate structures with it unless there have been objective calculations which demonstrate that the complete theory does in fact correctly predict structures and that the isolated term is dominant. Thus, in spite of the remarkable correlation of the above tendencies with experiment, they should be regarded as tentative. These considerations would strongly suggest in any case that an understanding of structures will require a careful explicit inclusion of hybridization, a conclusion already reached by Moriarty[10] in his study of the alkaline earths. This would explain the lack of success of our early studies[12] when they went below sodium, magnesium, and aluminum in the Periodic Table and also would explain what we believe to be lack of convincing correlation in more recent studies.[13] It would also explain the lack of success we obtained in adding third-order contributions in the model calculation mentioned earlier; the pseudopotential used was based upon that of Animalu and Heine,[11] which contains no explicit treatment of hybridization. The fact that the principal influence of the third order is restricted to the linear arrays of three ions, as well as the quantitative comparison with second order, would suggest that these three-ion interactions are essential.

Our studies also focus attention on backscattering form factors, a very different aspect of the pseudopotential from the form factors evaluated at the lattice wave numbers which entered the earlier studies of structure.[12,13] In principle it is correct that only the form factors at the lattice wave numbers affect the energy of a perfect crystal. However, the corresponding second-order energy turns out to vary only by 1% or so from structure to structure.

This does not mean that there is no hope for a second-order or low-order theory, since the higher orders are also quite insensitive to structure; it does mean that if we are to understand structures we must extract a subtle feature of the energy. The transformation to real space interactions does extract such a subtle feature. By separating off a different volume-dependent term, the resulting total interaction energy becomes comparable to the variation from structure to structure. This interaction, as we have seen, is dominated by the principal singularity, which in turn is associated with backscattering. It is not, for example, associated with the wave number where the form factor happens to go through zero. This feature is very much lost in the Fourier transform.

The influence of this same backscattering singularity on structure was explored earlier in the context of second-order theory by Shaw and by the present author.[14] Shaw calculated the total energy using the two-body asymptotic form of Eq. (17), an appreciable task. The resulting stability of hcp for $Z=1$, hcp (with bcc of essentially equal stability) for $Z=2$, and fcc for $Z=3$ was not so informative. The differences scale with the square of the backscattering form factor. We did not anticipate that the strongest contribution of the third-order terms would scale with the same factor. Indeed, the complete asymptotic form of the three-body interaction of Eq. (16) depends upon the sign and magnitude of the form factor at all angles. Because of this difference and because of the difference in the accuracy of the asymptotic forms in the two orders, it is not unreasonable to look at the influence of hybridization upon one order and not the other.

A careful test of this mechanism for structure determination is essential, but it is not easy. We have noted that in both second and third order the structure-dependent part of the energy is very small compared to the total. Further, that structure-dependent part is dominated by rather weak singularities. Thus any artificial singularities, such as the use of form factors with $|\vec{k}+\vec{q}|=k$ for $q<2k$ and $|\vec{k}+\vec{q}|=k+q$ for $q>2k$ or the use of artificial damping at large q, may completely invalidate the results. These may be avoided by making a full nonlocal calculation or by using an analytic local form for the unscreened form factor. However, it is not clear how this latter approach is best extended to hybridization. In addition, we must be certain that we have not utilized the inherent arbitrariness of all pseudopotential methods to obtain a desired result based upon an incorrect mechanism.

Note added in proof. We have recently found that selected terms in the n-ion interaction, which are of higher order than n in the pseudopotential, give rise to a phase shift in the interaction of Eq. (16). This adds a phase shift δ to the $k(l_1+l_2+\cdots l_n)$ which is the argument of the cosine. This phase shift for each path is the sum of phase shifts at each of the ions along the path. At each ion the shift is

$$\delta_{\text{ion}}=\frac{\Sigma_l(2l+1)\,\delta_l^2 P_l(\cos\theta)}{\Sigma_l(2l+1)\,\delta_l P_l(\cos\theta)}\ ,$$

where the δ_l are scattering phase shifts for electrons with the Fermi energy and θ is the angle made by the path at that ion. The special case for the two-body interaction has been given already by Heine and Weaire [V. Heine and D. Weaire, Solid State Phys. 24, 351 (1970)].

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