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Contribution of Core Polarization to the Cohesive Energies of the Alkali Metals

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An approximate potential is constructed to represent the effect of polarization of the atomic core on the energy of the valence electron in an atom with one valence electron. The potential is proportional to $1/R^4$ at large distances from the nucleus, but vanishes at the origin. The potential is treated in first-order perturbation theory to determine its contribution to the cohesive energies of the alkali metals. Numerical calculations have been made for lithium, sodium, and potassium. In the latter element, it represents about $\frac{1}{3}$ of the observed cohesive energy.

I. INTRODUCTION

FOR the alkali metals, it is a good approximation to consider the valence electron to be moving at a relatively large distance from a reasonably compact ionic core. In first approximation, the core can be assumed to be spherically symmetric so that the electric field external to it is the Coulomb field of the positive ion, characterized by the potential energy $-e^2/r$. This is not strictly accurate since the external electron distorts the core, inducing in it a dipole moment proportional to the polarizability of the ion. The field of the distorted core then reacts back on the valence electron, adding to its potential energy a term proportional to $e^2/2r^4$. The effect is an additional binding. Higher moments are also induced. Because the valence electron in the solid is, on the average, closer to the nucleus than in the free atom, there will be a contribution to the cohesive energy of the solid from the polarization effect.

The simple form of the effective polarization potential given above is valid only when the valence electron stays at a large distance from the core. Actually, the orbit of the valence electron penetrates the core. For an S state, the wave function of the valence electron is finite at the nucleus. The expectation value of the polarization potential, $\int|\psi|^2V_p d\tau$, is infinite for such a state because of the $1/r^4$ dependence of the potential. The object of this work is to give a more adequate treatment of the polarization effect by finding an effective polarization potential whose expectation value is finite for any state of the valence electron.

II. THE APPROXIMATE POTENTIAL

The development of a polarization potential in this section is based upon some work by Bethe[1] for a two-electron system. Suppose that a self-consistent field has been found for the positive ion of an alkali metal atom. We consider in perturbation theory the interaction of this atom and the valence electron. Under the influence of this perturbation, the Hartree-Fock one electron functions for the core electrons come to depend parametrically on the coordinates of the valence electron. The Hartree-Fock energy of the core also depends on the position of the valence electron. The equations for the core electrons are as follows (atomic units are used throughout the remainder of this paper):

$$\left[-\nabla_1^2+V(\mathbf{r}_1,\mathbf{r}_v)-A(\mathbf{r}_1,\mathbf{r}_v)+\frac{2}{r_{1v}}\right]u_i(\mathbf{r}_1,\mathbf{r}_v)=\epsilon_i(\mathbf{r}_v)u_i(\mathbf{r}_1,\mathbf{r}_v),\quad(1)$$

where

$$V(\mathbf{r}_1,\mathbf{r}_v)=-2Z/r_1+\sum_j\int|u_j(\mathbf{r}_2,\mathbf{r}_v)|^2\frac{2}{r_{12}}d\mathbf{r}_2,\quad(2)$$

and

$$A(\mathbf{r}_1,\mathbf{r}_v)f(\mathbf{r}_1,\mathbf{r}_v)=\sum_j\left(\int u_j^*(\mathbf{r}_2,\mathbf{r}_v)f(\mathbf{r}_2,\mathbf{r}_v)\frac{2}{r_{12}}d\mathbf{r}_2\right)u_j(\mathbf{r}_1,\mathbf{r}_v).\quad(3)$$

The quantities $\mathbf{r}_1$ and $\mathbf{r}_2$ are coordinate for core electrons; $\mathbf{r}_v$ is the coordinate of the valence electron. The approximation involved in Eq. (1) are discussed in the Appendix. The energy of the core is computed from these equations in the usual way. Exact solution of these equations will not be attempted. The quantity $2/r_{1v}$ will be treated as a perturbation according to the procedures of Allen[2] and Sternheimer.[3] Perturbation theory for the Hartree-Fock equations is quite complicated because of terms arising from altered Coulomb and exchange integrals. Allen has shown,[2] however, that the total energy E of the determinantal wave function can be written in perturbation theory as

$$E_C=E_0+E_1(\mathbf{r}_v)+E_2(\mathbf{r}_v),\quad(4)$$

where E_0 is the energy of the unperturbed determinantal function and E_1 and E_2 are given by:

$$E_1(\mathbf{r}_v)=\sum_i\int|u_i^{(0)}(\mathbf{r}_1)|^2\frac{2}{r_{1v}}d\mathbf{r}_1,\quad(5)$$

$$E_2(\mathbf{r}_v)=\sum_i\int u_i^{(0)*}(\mathbf{r}_1)\frac{2}{r_{1v}}u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v)d\mathbf{r}_1.\quad(6)$$

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[1] H. A. Bethe, in *Handbuch der Physik* (Edwards Brothers, Ann Arbor, 1943), Vol. 24, Part 1, pp. 339 ff.

[2] L. C. Allen, Bull. Am. Phys. Soc. Ser. II, **1**, 26 (1956). See also the Quarterly Progress Report of the Solid State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1955 (unpublished).

[3] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

The unperturbed functions $u_i^{(0)}$ satisfy

$$[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)]u_i^{(0)}(\mathbf{r}_1)=\epsilon_i^{(0)}u_i^{(0)}(\mathbf{r}_1), \quad (7)$$

where $V(\mathbf{r}_1)$ and $A(\mathbf{r}_1)$ are constructed analogously to (2) and (3). The first-order perturbed functions $u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v)$ satisfy[2]

$$\begin{aligned}[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^{(0)}]u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v) \\ =(\epsilon_i^{(1)}-2/r_{1v})u_i^{(0)}(\mathbf{r}_1) \\ -\sum_j\left\{\int u_j^{(0)*}(\mathbf{r}_2)u_j^{(1)}(\mathbf{r}_2,\mathbf{r}_v)\frac{2}{r_{12}}d\mathbf{r}_2\right. \\ \left.+\int u_j^{(1)*}(\mathbf{r}_2,\mathbf{r}_v)u_j^{(0)}(\mathbf{r}_2)\frac{2}{r_{12}}d\mathbf{r}_2\right\}u_i^{(0)}(\mathbf{r}_1) \\ +\sum_j\left\{\int u_j^{(1)*}(\mathbf{r}_2,\mathbf{r}_v)u_i^{0}(\mathbf{r}_2)\frac{2}{r_{12}}d\mathbf{r}_2u_j^{(0)}(\mathbf{r}_1)\right. \\ \left.+\int u_j^{(0)*}(\mathbf{r}_2)u_i^{(0)}(\mathbf{r}_2)\frac{2}{r_{12}}d\mathbf{r}_2u_j^{(1)}(\mathbf{r}_1,\mathbf{r}_v)\right\}, \quad (8)\end{aligned}$$

where

$$\begin{aligned}\epsilon_i^{(1)}(\mathbf{r}_v)=\int|u_i^{(0)}(\mathbf{r}_1)|^2\frac{2}{r_{1v}}d\mathbf{r}_1 \\ +\sum_j\left\{\int u_j^{(1)*}(\mathbf{r}_1,\mathbf{r}_v)u_i^{(0)*}(r_2)\frac{2}{r_{12}}u_j^{(0)}(\mathbf{r}_1)u_i^{(0)}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\right. \\ +\int u_j^{(0)*}(r_1)u_i^{(0)*}(\mathbf{r}_2)\frac{2}{r_{12}}u_j^{(1)}(\mathbf{r}_1,\mathbf{r}_v)u_i^{(0)}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \\ -\int u_j^{(1)*}(\mathbf{r}_1,\mathbf{r}_v)u_i^{(0)*}(\mathbf{r}_2)\frac{2}{r_{12}}u_j^{(0)}(\mathbf{r}_2)u_i^{(0)}(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2 \\ \left.-\int u_j^{(0)*}(\mathbf{r}_1)u_i^{(0)*}(\mathbf{r}_2)\frac{2}{r_{12}}u_j^{(1)}(\mathbf{r}_2,\mathbf{r}_v)u_i^{(0)}(r_1)d\mathbf{r}_1d\mathbf{r}_2\right\}. \quad (9)\end{aligned}$$

These equations are too complicated to solve. We drop all the perturbed Coulomb and exchange integrals from Eqs. (8) and (9) so that they reduce to the ordinary forms of perturbation theory:

$$\begin{aligned}[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^{(0)}]u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v) \\ =(\epsilon_i'^{(1)}(\mathbf{r}_v)-2/r_{1v})u_i^{(0)}(\mathbf{r}_1), \quad (10)\end{aligned}$$

where

$$\epsilon_i'^{(1)}(\mathbf{r}_v)=\int|u_i^{(0)}(\mathbf{r}_1)|^2\frac{2}{r_{1v}}d\mathbf{r}_1. \quad (11)$$

The error involved in eliminating the offending terms is discussed in Sec. VI where it is shown to be reasonably small. Equation (10) is still too difficult to solve, since it contains all multipole orders. We expand $1/r_{1v}$ in spherical harmonics in the standard way and obtain:

$$\begin{aligned}\frac{1}{r_{1v}}=\frac{1}{r_1}+\frac{r_v}{r_1^2}\cos\theta+\frac{r_v^2}{2r_1^3}(3\cos^2\theta-1)+\cdots \text{ for } r_1>r_v, \\ \frac{1}{r_{1v}}=\frac{1}{r_v}+\frac{r_1}{r_v^2}\cos\theta+\frac{r_1^2}{2r_v^3}(3\cos^2\theta-1)+\cdots \text{ for } r_v>r_1.\end{aligned} \quad (12)$$

In (12), θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_v$.

The term in (12) proportional to $\cos\theta$ yields the ordinary dipole polarization; the term proportional to $(3\cos^2\theta-1)$ gives a quadrupole term, and so on. We terminate the series after the second term. The order of magnitude of the quadrupole effect will be considered in Sec. V for a simple case.

If we substitute (12) in (5), we see that the expectation values of all the terms except the spherically symmetric one vanish. We obtain

$$E_1=\sum_i\epsilon_i'^{(1)}=\sum_i\left[\frac{2}{r_v}\int_0^{r_v}|u_0(\mathbf{r}_1)|^2d\mathbf{r}_1+\int_{r_v}^{\infty}|u_0(\mathbf{r}_1)|^2\frac{2}{r_1}d\mathbf{r}_1\right]. \quad (13)$$

In finding the second-order perturbation according to (6) and (10), we may neglect the contribution from the spherically symmetric part and from $\epsilon_i'^{(1)}$, since it is known from self-consistent field studies of neutral atoms of the alkali metals[4] that the spherically symmetric part of the potential of the valence electron produces little change in the wave functions of the core electrons.

To obtain the change in the wave functions of the core electrons, we now have to solve the pair of differential equations:

$$\begin{aligned}[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^{(0)}]u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v) \\ =-\frac{2r_1}{r_v^2}\cos\theta u_i^{(0)}(\mathbf{r}_1) \quad \text{for} \quad r_v>r_1, \\ [-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^{(0)}]u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v) \\ =-\frac{2r_v}{r_1^2}\cos\theta u_i^{(0)}(\mathbf{r}_1) \quad \text{for} \quad r_1>r_v.\end{aligned} \quad (14)$$

The solutions must then be joined on the boundary $r_1=r_v$. This is a very difficult task unless fast electronic computing equipment is available. The assumption now is made that the fraction of time the core electron is outside the valence electron can be neglected: in other words, we consider only the region $r_v>r_1$ and neglect the region $r_1>r_v$. This assumption is plausible on physical grounds. It will be examined further in Sec. III, where a comparison is made with the work of

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[4] See, for instance, the treatment of neutral K and of K⁻: D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc. **34**, 550 (1938).

Bethe[1] in which both regions are considered for a simple case. The equation which actually is used is:

$$[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^{(0)}]u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v)=-\frac{2r_1}{r_v^2}\cos\theta u_i^{(0)}(\mathbf{r}_1). \quad (15)$$

Reasonable approximations to solutions of this equation have been found for a number of cases by Sternheimer.[5] They are used in this work.

The perturbed wave functions are then used to calculate the Hartree-Fock energy of the perturbed core according to (4), (6), and (13). This energy is a function of $\mathbf{r}_v$. It can be used as a potential energy function for the valence electron. The valence electron wave function $\psi(\mathbf{r}_v)$ satisfies the equation:

$$[-\nabla_v^2-2Z/r_v+E_C(\mathbf{r}_v)]\psi(\mathbf{r}_v)=\epsilon\psi(\mathbf{r}_v), \quad (16)$$

where $E_C(\mathbf{r}_v)$ is the energy of the core and ϵ is the total energy of the system: core plus valence electron. A derivation of this equation is given in the Appendix. It is seen from (13) that the first-order perturbation of the core gives the screening of the nuclear charge by the core electrons. Core valence exchange has been neglected in obtaining (16). The term $E_2(\mathbf{r}_v)$ is the polarization potential that is desired. It will be called $V_p(\mathbf{r}_v)$ from now on, and according to (6) in the approximation of neglecting the region $r_1>r_v$ is given by

$$V_p(\mathbf{r}_v)=\left(\frac{2}{r_v^2}\right)\sum_i\int_0^{r_v}u_i^{(0)*}(\mathbf{r}_1)r_1\cos\theta u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v)d\mathbf{r}_1. \quad (17)$$

The potential must represent an additional binding since the inclusion of the valence electron coordinates in the core wave functions is an improvement of the total wave function of the system. In applying (16) to the cases of interest, we use perturbation theory and treat V_p as a perturbation on self-consistent-field wave functions for the atoms and solids studied.

III. COMPARISON WITH BETHE'S SOLUTION

In order to test the validity of the approximation which neglects the region $r_1>r_v$, the polarization potential obtained according to (17) was compared, in a simple case, with the result of Bethe's treatment[1] in which the region $r_1>r_v$ is not discarded. We consider the case of polarization of the 1*s* electron shell in a situation where the unperturbed wave function of these electrons is proportional to e^{-Zr}. This is true only when the potential of the core electrons is $-2Z/r$, but fair accuracy can be obtained for helium and lithium (in the latter case, variational wave functions can be used[6]). When the core function is so simple, the perturbed wave function can easily be found analytically.[3] The approximate polarization potential computed according to (17) is, when one considers two 1*s* electrons:

$$V_p(x)=\frac{-9}{x^4}\left[1-e^{-2x}\left(1+2x+2x^2+\frac{4}{3}x^3+\frac{2}{3}x^4+\frac{4}{27}x^5\right)\right], \quad (18)$$

where $x=Zr_v$. For comparison, the result obtained by Bethe[1] is:

$$V_p(x)=\frac{-9}{x^4}\left[1-\frac{1}{3}e^{-2x}\left(1+2x+6x^2+\frac{20}{3}x^3+\frac{4}{3}x^4\right)-\frac{2}{3}e^{-4x}(1+x)^4\right]. \quad (19)$$

These potentials are shown in Fig. 1 for $Z=2.69$, the variational parameter for lithium.[6] The result of the simple approximation of the introduction would be just $V_p(x)=9/x^4$. Near the nucleus, the potentials (18) and (19) can be expanded in power series. The potential of Eq. (18) begins like $-(16/15)x$, whereas Bethe's potential begins like $-(8/3)x^2$.

To compare the two approximations further, the expectation values of (18) and (19) were found using an approximate wave function for the 2*s* state of the lithium atom. The approximation proposed here, Eq. (18) gave an average polarization energy of 0.00621 rydberg, while the more accurate expression, (19) gave 0.00651 rydberg. The difference amounts to 4.6% of the latter value. We may conclude from this comparison that the proposed approximation is satisfactory.

IV. APPLICATIONS TO THE ALKALI METALS

Sternheimer has obtained solutions to Eq. (15) for some states of electrons in lithium, sodium, and potassium. These functions were used to compute the approximate polarization potential according to (17). Self-consistent-field functions were used for the unper-

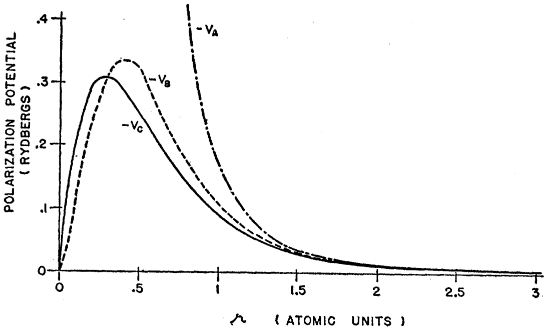

FIG. 1. Comparison of approximate polarization potentials, for lithium. V_C is the approximate potential computed according to (17); V_B is that computed by Bethe (Eq. 19); and V_A is the asymptotic potential $9/x^4$, where $x=Zr$. ($z=2.69$)

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[5] I am indebted to Dr. Sternheimer for furnishing me with tables of his perturbed wave functions.

[6] Morse, Young, and Haurwitz, Phys. Rev. 48, 948 (1935).

turbed core functions.[7] The polarization potentials so obtained are given in Table I.

To determine the effect of $V_p(r)$ on the cohesive energies of the alkali metals, we have recourse again to perturbation theory. First-order perturbation theory was used, and expectation values of V_p were found for the valence electron in the free atom as well as in the solid. The average value in the solid will tend to be larger in magnitude than in the free atom since the valence electron in the solid is confined to the atomic polyhedron. Self-consistent-field wave functions were used for the ground state of the valence electron in the free atom.[8] For the solid, the expectation values must be found to order k^2, and to do this, wave functions correct to order k^2 must be used. The functions for lithium were obtained from Kohn,[9] the ones for sodium were computed by us from the empirical Prokofjew potential given by Wigner and Seitz,[10] and those for potassium were obtained from our previous work on this element.[11] The results are given in Table II. It is interesting to see that the large contribution of 8.7 kcal/mole in potassium amounts to 37% of the observed cohesive energy. This large value is required to offset the effect of the k^4 terms on the Fermi energy,[12] so that the cohesive energy is approximately given by the standard procedure. Similar large values of the polarization effect may be expected for rubidium and cesium. The compensation with the k^4 terms may also occur for these.

TABLE I. Polarization potentials for lithium, sodium, and potassium. The potentials all are negative (binding) for large r, and are given in atomic units. (1 atomic unit≡2 rydbergs.) The repulsive part of the potassium potential is presumably due to neglect of the region $r_1 > r_v$. It does not make a large contribution to the average polarization energy because the valence electron wave function is small in the interior of the core. The radius r is given in units of the Bohr radius a_H.

Radius (r)	$-V_p$(Li)	$-V_p$(Na)	$-V_p$(K)
0.00	0.0000	0.0000	0.0000
0.01		0.10	0.69
0.02	0.0567	0.28	1.14
0.03		0.56	1.39
0.04	0.1144	0.99	1.49
0.05		1.18	1.38
0.06	0.1538	1.331	1.17
0.07		1.349	0.861
0.08	0.1856	1.344	0.636
0.09		1.321	0.414
0.10	0.2151	1.286	+0.220
0.15	0.2693	0.9037	−0.4707
0.20	0.2999	0.5631	−0.7283
0.25	0.3132	0.3831	−0.6893
0.30	0.3134	0.2360	−0.5463
0.35	0.3068	0.1161	−0.3908
0.40	0.2942	0.0700	−0.2471
0.50	0.2593	0.0517	−0.0162
0.60	0.2207	0.0871	+0.1534
0.70	0.1835	0.1307	0.2789
0.80	0.1505	0.1610	0.3770
0.90	0.1222	0.1755	0.4464
1.00	0.0987	0.1771	0.4913
1.10	0.0798	0.1698	0.5133
1.20	0.0690	0.1573	0.5175
1.40	0.0417	0.1257	0.4875
1.60	0.0274	0.0958	0.4292
1.80	0.0184	0.0709	0.3621
2.00	0.0126	0.0520	0.2968
2.5	0.0054	0.0243	0.1686
3.0	0.0026	0.0122	0.0947
3.5	0.0014	0.0066	0.0547
4.0	0.0008	0.0039	0.0330
4.5	0.0005	0.0024	0.0208
5.0	0.0003	0.0016	0.0137
6.5	0.0002	0.0011	0.0094
6.0	0.0002	0.0008	0.0066
6.5	0.0001	0.0006	0.0048
7.0	0.0001	0.0004	0.0036

TABLE II. Effect of the polarization potential. Average values of the polarization potential are given in rydbergs for lithium, sodium, and potassium. The change in the effective mass and the cohesive energy is also given. The effect always is to increase the cohesive energy.

	Lithium	Sodium	Potassium
Average value (free atom)	−0.0075	−0.0130	−0.0353
Average value (lowest valence state in solid)	−0.0170	−0.0194	−0.0595
Change in effective-mass ratio (m/m^*)	+0.0094	−0.0055	−0.0372
Change in the cohesive energy (kcal/mole)	2.34	2.24	8.66

An estimate of the error introduced by using first-order perturbation theory to determine the effect of V_p on the valence electron energy was made by integrating the appropriate equation to determine the first-order perturbation of the wave function, and thus the second-order perturbation of the energy for the lowest state, Γ_1, of the valence electron in potassium. The energy of that state decreased in second order by 5.6%. We may conclude that first-order perturbation theory is satisfactory.

In the case when the cohesive energy of the solid is calculated on the basis of a self-consistent field, as for potassium,[11] it is clear that the effect of polarization must be added to the result previously reported. For lithium and sodium, calculations have been based on empirical potentials which reproduce the spectroscopic term values. In these cases, the effect of polarization is presumably contained in the empirical potentials. In the quantum defect method, a correction for polar-

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[7] For sodium and lithium, the wave functions of P. O. Löwdin, Phys. Rev. **90**, 120 (1953), were used; for potassium, the wave functions were taken from D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1936).

[8] Lithium: V. Fock and M. J. Petrashen, Physik Z. Sowjetunion, **8**, 547 (1935). Sodium: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948). For potassium, see reference 4.

[9] W. Kohn (private communication).

[10] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[11] Berman, Callaway, and Woods, Phys. Rev. **101**, 1467 (1956).

[12] J. Callaway, Phys. Rev. **103**, 1219 (1956).

ization must also be applied,[13] but its magnitude has not been calculated. It need not be the same as that obtained here.

V. QUADRUPOLE POLARIZATION

The same approximation introduced in the study of dipole polarization can be applied to the quadrupole polarization, which results from the terms in (12) proportional to $(3\cos^2\theta-1)$. Again, we consider only the region $r_v>r_1$. We add a term to the wave function of the core to represent the quadrupole distortion. This term, $u_i^{(2)}(\mathbf{r}_1,\mathbf{r}_v)$, satisfies, by analogy

$$[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)-\epsilon_i^0]u_i^{(2)}(\mathbf{r}_1,\mathbf{r}_v) =\left[\epsilon_i^{(2)}(\mathbf{r}_v)-\frac{r_1^2}{r_v^3}(3\cos^2\theta-1)\right]u_i^{(0)}(\mathbf{r}_1). \quad (20)$$

Here

$$\epsilon_i^{(2)}=\int|u_i^{(0)}(\mathbf{r}_1)|^2\frac{r_1^2}{r_v^3}(3\cos^2\theta-1)d\mathbf{r}_1. \quad (21)$$

The quantity $\epsilon_i^{(2)}$ vanishes for an S state, but not for P and D states, etc. At first sight, this would seem to lead to a term in the potential energy proportional to $1/r_v^3$, which would be of greater magnitude than the dipole term. It is easy to show, however, that if $\epsilon_i^{(2)}$ is summed over all the levels characterized by different values of the magnetic quantum number m belonging toa closed shell of definite l, the sum vanishes. We can proceed to calculate the quadrupole polarization potential in a manner similar to (17).

$$V_q(\mathbf{r}_v)=\frac{1}{r_v^3}\sum_i\int_0^{r_v}u_i^{(0)*}(\mathbf{r}_1)r_1^2(3\cos^2\theta-1)\times u_i^{(2)}(\mathbf{r}_1,\mathbf{r}_v)d\mathbf{r}_1. \quad (22)$$

At large r_v, the potential is proportional to $1/r_v^6$. For the situation of Sec. III, V_q has the form

$$V_q(x)=-\frac{30}{x^6}\left[1-e^{-2x}\left(1+2x+2x^2+\frac{4}{3}x^3+\frac{2}{3}x^4+\frac{4}{15}x^5+\frac{4}{45}x^6+\frac{4}{225}x^7\right)\right], \quad (23)$$

where $x=Zr$. For small x, V_q begins as $-(8/35)x$. In spite of the $(1/x^6)$ term, the function V_q is linear in x at the origin. It follows that a representation of the quadrupole potential as just $-\alpha_q/r_v^6$, where α_q is the quadrupole polarizability, may give a considerable overestimate of the polarization energy even for states for which the expectation value of r^{-6} is finite.

The quadrupole polarization potential, V_q, has been evaluated for lithium using the variational wave functions mentioned in Sec. III. The expectation value of this potential has been found for both the free lithium atom and the metal. It lowers the energy of the valence electron in the free atom by about 0.001 rydberg and increases the cohesive energy by about 0.4 kcal/mole. This is about 20% of the contribution from the dipole polarization. It would appear from this that the sum of the effects of the several terms of the series (12) does not converge with great rapidity.

There are, however, other effects proportional to r^{-6} for large r. Such terms would come, for instance, from a third-order calculation of dipole polarization and from the kinetic energy correction to be discussed in the Appendix. The existence of these effects, whose magnitudes are not well known at present, limits the accuracy possible in a calculation of cohesive energies from self-consistent fields.

All of the effects discussed in this paper pertain to the so-called correlation between valence and core electrons. It appears that much of this correlation energy can be developed in a series of terms forming an effective potential; the terms in this series are proportional to r_v^{-2n} at large r_v, where n is an integer greater than 2. The major part of the r_v^{-4} term is the dipole polarization, which can be approximately evaluated; the other terms remain obscure. It is probably impossible, however, to expand the entire correlation energy in this way, since the derivation of Eq. (1) as given in the Appendix involves certain approximations.

VI. EFFECT OF NEGLECT OF PERTURBED COULOMB AND EXCHANGE INTEGRALS IN PERTURBATION THEORY

We consider now the effect on the energy of the inclusion of the perturbed Coulomb and exchange integrals into the equation of first-order perturbation theory. To estimate this, we evaluate the integral occurring in Eq. (8) which we call ΔV_c:

$$\Delta V_c=\sum_j\int u_j^{(0)*}(\mathbf{r}_2)\frac{2}{r_{12}}u_j^{(1)}(\mathbf{r}_2,\mathbf{r}_v)d\mathbf{r}_1. \quad (24)$$

We use for $u_j^{(1)}$ the perturbed wave function calculated

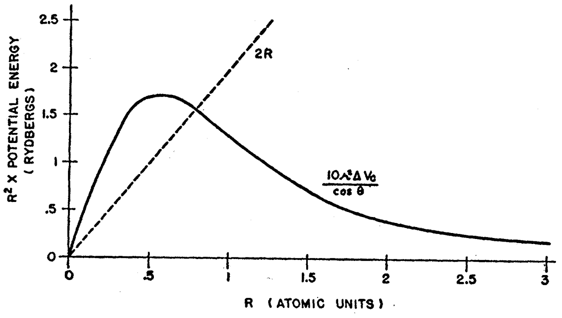

FIG. 2. Comparison of ten times the perturbed Coulomb integral, (25), with the perturbation of the valence electron. Both functions are multiplied by $r_v^2\sec\theta$ to obtain a function of $r_1=R$ only.

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[13] F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

previously by Sternheimer neglecting such terms. The calculation is performed for lithium using the analytic, approximate, wave functions of Sec. III. We find

$$\Delta V_c=\frac{9\cos\theta}{r_1^2r_v^2Z^4}\left\{1-e^{-2Zr_1}\left[1+2Zr_1+2(Zr_1)^2+\frac{34}{27}(Zr_1)^3+\frac{2}{9}(Zr_1)^4\right]\right\}. \quad (25)$$

In order to obtain an estimate of the influence of this term, it should be compared with the perturbation previously considered: $(2r_1/r_v^2)\cos\theta$. This comparison is shown in Fig. 2. We see that ΔV_c has only a small influence except at the origin. If greater accuracy is desired, it would seem possible to treat Eq. (8) by iteration: by solving it without the perturbed Coulomb and exchange integrals, and then treating such integrals as additional perturbations.

VII. ACKNOWLEDGMENTS

I am indebted to Dr. Morrel H. Cohen for valuable discussions. D. E. Jack, E. L. Haase, and B. Rothman assisted with the computations.

APPENDIX. DERIVATION OF EQS. (1) AND (16)

We consider a single free atom of the substance of interest, and separate the valence and core electrons by writing the total wave function of the system as

$$\Psi(\mathbf{r}_c,\mathbf{r}_v)=\Phi(\mathbf{r}_c,\mathbf{r}_v)\psi(\mathbf{r}_v), \quad (26)$$

where $\mathbf{r}_c$ stands for the coordinates of the core electrons and $\mathbf{r}_v$ for those of the valence electron. ψ is the wave function of the valence electron and Φ that of the core electrons. By using an approximation of the form (26) which is not antisymmetric between valence and core electrons, we neglect valence core exchange. The polarization potential derived from the equations below is regarded as approximating that derived from an antisymmetric function. Φ is considered to depend parametrically on the valence electron coordinates. ψ and Φ are normalized individually; the latter for all values of $\mathbf{r}_v$.

The Hamiltonian for the system is:

$$H=H_c(\mathbf{r}_c)+H_v(\mathbf{r}_v)+H_i(\mathbf{r}_c,\mathbf{r}_v), \quad (27)$$

where H_c is the Hamiltonian for the core electrons unperturbed by the valence electrons, H_v is the Hamiltonian for the valence electron, and H_i gives the interaction between the valence and core electrons.

$$H_c(\mathbf{r}_c)=\sum_{i=1}^{Z-1}\left(-\nabla_i^2+2\frac{Z}{r_i}+\sum_{j>i}\frac{2}{r_{ij}}\right),$$

$$H_v(\mathbf{r}_v)=-\nabla_v^2-2\frac{Z}{r_v}, \quad (28)$$

$$H_i(\mathbf{r}_c,\mathbf{r}_v)=\sum_{i=1}^{Z-1}\frac{2}{r_{iv}}.$$

The equation satisfied by the function (26) is:

$$(H_c+H_v+H_i)\psi\Phi=\epsilon\psi\Phi. \quad (29)$$

We multiply (29) by Φ^* and integrate over coordinates r_c.

$$\left[\int\Phi^*(H_c+H_i)\Phi d\mathbf{r}_c\right]\psi(\mathbf{r}_v)+\int\Phi^*H_v(\psi(\mathbf{r}_v)\Phi(\mathbf{r}_c,\mathbf{r}_v))d\mathbf{r}_c=\epsilon\psi(r_v). \quad (30)$$

Suppose now that Φ satisfies the following equation:

$$[H_c(\mathbf{r}_c)+H_i(\mathbf{r}_c,\mathbf{r}_v)]\Phi=E_c(\mathbf{r}_v)\Phi. \quad (31)$$

Substitute (31) into (30) and make use of the normalization of Φ for all $\mathbf{r}_v$. The equation satisfied by ψ is then obtained.

$$\left[\int\Phi^*H_v(\Phi\psi)d\mathbf{r}_c\right]=[\epsilon-E_c(\mathbf{r}_v)]\psi. \quad (32)$$

We now introduce the explicit valence electron Hamiltonian. Observe that

$$\int\Phi^*H_v(\Phi\psi)dr_c=\left(-\nabla_v^2-\frac{2Z}{r_v}\right)\psi+\left[\int\Phi^*(-\nabla_v^2\Phi)dr_c\right]\psi.$$

We have made use of the Hermitian properties of the operator $(1/i)\nabla$. Then (32) becomes:

$$\left[-\nabla_v^2-\frac{2Z}{r_v}\right]\psi=\left[\epsilon-E_c(\mathbf{r}_v)-\int\Phi^*(-\nabla_v^2\Phi)dr_c\right]\psi. \quad (33)$$

The function $E_c(\mathbf{r}_v)$ obtained as the eigenvalue of (31) is seen to play the role of an additional potential. It contains the desired polarization potential.

We now make the determinantal approximation for Φ. We write

$$\Phi=\det|u_i(\mathbf{r}_j,\mathbf{r}_v)|. \quad (34)$$

Standard procedures then lead us to the Hartree-Fock equations to determine the functions $u_i(\mathbf{r}_j,\mathbf{r}_v)$ in such a way that the energy of the core is minimized for all $\mathbf{r}_v$. The function E_c can now be interpreted as the Hartree-Fock energy of the system. The Hartree-Fock equations obtained in this way are Eqs. (1).

Equation (16) is obtained from (33) by dropping the kinetic energy correction $\int\Phi^*(-\nabla_v^2\Phi)dr_c$. This correction has the effect of an additional potential since it is a function of $\mathbf{r}_v$. Because the kinetic energy is an inherently positive quantity, the correction has opposite sign to the polarization potential. We investigate it further by making the determinantal approximation for Φ. Its elements $u_i(\mathbf{r}_j,\mathbf{r}_v)$ in fact are constructed according to the equation of perturbation theory (15).

The kinetic energy correction is investigated within perturbation theory. We observe that $-\nabla_v^2$ is of the order $1/r_v^2$; i.e., it is of the same size as the perturbing Hamiltonian in (25). If we expand the determinantal function Φ, we find that

$$\int \Phi^*(-\nabla_v^2\Phi)d\mathbf{r}_c=\sum_i\int u_i^{(0)*}(\mathbf{r}_1)(-\nabla_v^2 u_i^{(1)}(\mathbf{r}_1,\mathbf{r}_v))d\mathbf{r}_1 +O(1/r_v^6). \quad (35)$$

The first term is of the order $1/r_v^4$ since $u_i^{(1)}$ is proportional to $1/r_v^2$. Terms of the order $1/r_v^6$ and higher are neglected here, but would have to be included in an evaluation of quadrupole terms. The $1/r_v^4$ term in (35) appears to be of the same order as V_p. Upon substitution of the perturbed wave functions $u_i^{(1)}$ into (35), it is found that the integral vanishes upon integration over solid angle. Consequently there is no contribution from the kinetic energy correction of the same order in r_v as the dipole polarization potential.

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Plasma Losses by Fast Electrons in Thin Films*

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The angle-energy distribution of a fast electron losing energy to the conduction electrons in a thick metallic foil has been derived assuming that the conduction electrons constitute a Fermi-Dirac gas and that the fast electron undergoes only small fractional energy and momentum changes. This distribution exhibits both collective interaction characteristics and individual interaction characteristics, and is more general than the result obtained by other workers. Describing the conduction electrons by the hydrodynamical equations of Bloch, it has been shown that for very thin idealized foils energy loss may occur at a value which is less than the plasma energy, while as the foil thickness decreases below $\sim v/\omega_p$ the loss at the plasma energy becomes less than that predicted by more conventional theories. The net result is an increase in the energy loss per unit thickness as the foil thickness is decreased. It is suggested that the predicted loss at subplasma energies may correspond to some of the low-lying energy losses which have been observed by experimenters using thin foils.

I. INTRODUCTION

THERE has been recently a rather extraordinary amount of experimental and theoretical work on the origin and implications of characteristic energy losses experienced by fast electrons in passing through foils. This effort has received great impetus from the suggestion by Pines and Bohm[1] that some of these energy losses are due to the excitation of plasma oscillations or "plasmons" in the sea of conduction electrons and from their work on the theory of these oscillations.[2] An alternate explanation, which has been advanced many times by various workers, is that these losses are due to interband transitions of individual conduction electrons. Evidence in support of this has been presented[3] showing correlation between the fine structure of x-ray absorption edges and the characteristic loss lines. The plasma interpretation has been strengthened by Watanabe's[4] experimental verification of the Pines-Bohm plasma dispersion relation [Eq. (12) below] in Be, Al, Mg, and Ge. A critical review of the present status of the theory and experiment in this field has been given by Pines.[5]

It is the purpose of this paper to examine theoretically the energy and angular distribution of a fast electron which has lost energy to plasma oscillations in an infinite foil and to consider the effect of the finiteness of the foil. Ferrell[6] has investigated the angular dependence of the characteristic energy losses of fast electrons to an infinite plasma using the theory of Pines and Bohm.[2] He obtains one formula which involves the collective interaction of conduction electrons with the incident electrons and another which includes only the effect of individual interactions between conduction electrons and the incident electrons. A single formula will be derived which includes both collective and individual interactions and which depends upon the momentum distribution of the undisturbed plasma.

Gabor[7] has considered the interaction of a fast electron with a small metallic crystal containing free electrons. He assumes that the electric field is always zero at the surface of the crystal and examines the

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