

trations larger than $2 \times 10^{16}/\text{cc}$ and smaller than about $10^{17}/\text{cc}$.

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Cohesive Energy of Noble Metals

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The method, developed by Kuhn and Van Vleck, and later simplified and extended by Brooks, for calculating the cohesive energy of monovalent metals, is here further extended to include the effects of the deviation of the effective ion-core potential from pure hydrogenic form in the vicinity of the surface of the s -sphere. A formula is derived for calculating the logarithmic derivative of the wave function at the surface of the s -sphere. From the logarithmic derivatives of the s - and p -functions the ground-state energy and the Fermi energy can be evaluated. The method thus extended is applied to the calculation of the cohesive energy of the monovalent noble metals. For these metals, the repulsion between ion cores is important. Combining the repulsive energy, which is

calculated by Fuchs with a modified Thomas-Fermi method, with the energy of valence electrons calculated by the present method, we obtain the total cohesive energy of copper. Since there is no calculation of the repulsive energy for silver and gold, the ion cores are assumed to be rigid and the energies of the valence electrons at the observed lattice spacings are determined and considered as the approximate total energies. The cohesive energies calculated at the observed lattice spacings with the rigid ion-core assumption are 61.7 for Cu, 55.8 for Ag, and 49.2 for Au in comparison with the experimental values of 81.2, 68.0, and 92.0 respectively. Here the energy unit is kcal/mole.

1. INTRODUCTION

VAN VLECK and Kuhn¹ have given simplified methods of calculating the cohesive energies of monovalent metals. Recently, Brooks² has pointed out a number of simplifications of their methods and obtained reasonable theoretical predictions of the cohesive energy and lattice constants of all the alkali metals. The Van Vleck-Kuhn method is based on the following facts: (1) The effective potential in the vicinity of the surface of the s -sphere in the Wigner-Seitz sphere approximation³ is essentially hydrogenic, therefore, (2) the wave function in the same region can be excellently approximated by a linear combination of the confluent hypergeometric functions, *viz.*,

$$U_h^{(l,n)}(r) = \bar{W}^{(l,n)}(r) + k_l \tilde{W}^{(l,n)}(r), \quad (1)$$

where the functions $\bar{W}^{(l,n)}$ and $\tilde{W}^{(l,n)}$ are related to the standard Whittaker functions by Eqs. (11a, b) in Van Vleck and Kuhn, and (3) k_l can be determined by the function matching method. Brooks, however, has shown that

$$k_l = -\tan(\delta_l \pi), \quad (2)$$

where δ_l is the quantum defect.

In the present paper, the cohesive energy of the noble

metals will be computed by the Brooks method, incorporating the correction due to the deviation of the effective potential from the pure hydrogenic form. In the case of copper, Fuchs⁴ has calculated the cohesive energy by numerical integration of the radial wave equation in a Hartree-Fock potential. His results for copper as well as the observed values for all noble metals will be compared with our results in the last section.

2. EXTENSION OF THE BROOKS METHOD

We shall first explain a further extension of the Brooks method of determining k_l , and then derive the expression for the logarithmic derivative of the wave function with the correction due to the deviation of the effective potential from the pure hydrogenic form.

In calculating s - as well as p -functions by (1) and (2), Brooks has determined the dependence of δ_l on the energy ϵ by straight forward extrapolation from the free atom term values for both s - and p -levels. For s -levels, $l=0$, the straightforward extrapolation of δ_0 is legitimate and nearly linear in most cases. For $l \geq 1$, however, Ham⁵ has pointed out that the straight-forward extrapolation of δ_l is often not adequate. Instead of δ_l the quantity η_l , which is related to δ_l by

$$\tan(\eta_l \pi) = \frac{\tan(\delta_l \pi)}{1 + \epsilon}, \quad (3)$$

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¹ J. H. Van Vleck and T. S. Kuhn, Phys. Rev. **79**, 382 (1952).

² H. Brooks, Phys. Rev. **91**, 1027 (1953).

³ E. P. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

⁴ K. Fuchs, Proc. Roy. (London) **A151**, 585 (1935).

⁵ F. Ham (private communication).

should be extrapolated in case of $l=1$. If the x-ray term values or the energy parameters in the self-consistent field equation of Hartree-Fock type are known, these energy values will give further information on the dependence of η_1 on ϵ .⁶ For alkali metals, the wave function calculated by (1) with (2) yields excellent results for the usual solid-state parameters, if we carry out the δ_0 and η_1 extrapolation for s - and p -functions, respectively.

For monovalent noble metals, however, the effective potential in the vicinity of the surface of the s -sphere is not completely hydrogenic, because the actual lattice spacings of these metals are relatively small. Therefore, the wave function also is not purely hydrogenic, and we have to make corrections due to the deviation of the effective potential from the pure hydrogenic form in this region. These corrections can be obtained in the following way.⁷

In calculating the ground-state energy ϵ_0 and the Fermi energy ϵ_F , we need only the knowledge of the logarithmic derivatives of the s - and p -functions, if we take only the first two terms of the expansion of the energy in powers of \hbar . Hence, we shall derive the corrected expression of the logarithmic derivative of the wave function.

The uncorrected wave function $U_h^{(l,n)}(r)$ satisfies the radial wave equation with the pure hydrogenic potential:

$$\frac{d^2 U_h^{(l,n)}}{dr^2} + \left[-\frac{1}{n^2} + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] U_h^{(l,n)} = 0, \quad (4)$$

where $1/n^2 = -\epsilon$. The true wave function $U^{(l,n)}(r)$ should satisfy the wave equation with the true effective potential $V(r)$:

$$\frac{d^2 U^{(l,n)}}{dr^2} + \left[-\frac{1}{n^2} - V(r) - \frac{l(l+1)}{r^2} \right] U^{(l,n)} = 0. \quad (5)$$

Here and elsewhere, the energy is in Rydberg units, and r is in Bohr units. We assume that the potential $V(r)$ and the wave function $U^{(l,n)}(r)$ become essentially hydrogenic for all $r > R$. From (4) and (5), we find that

$$\int_{r_s}^R \left[\frac{d^2 U_h^{(l,n)}}{dr^2} U^{(l,n)} - U_h^{(l,n)} \frac{d^2 U^{(l,n)}}{dr^2} \right] dr \\ = - \int_{r_s}^R \left[\frac{2}{r} + V(r) \right] U_h^{(l,n)} U^{(l,n)} dr, \quad (6)$$

where r_s is the radius of the s -sphere. By integration by

⁶ The use of η_1 and of the deep-lying levels was suggested by H. Brooks.

⁷ The procedure described in the following paragraphs was worked out by H. Brooks, to whom I am indebted for the loan of his notes on the method.

parts, (6) can be reduced to

$$U^{(l,n)} \frac{dU_h^{(l,n)}}{dr} - U_h^{(l,n)} \frac{dU^{(l,n)}}{dr} \Big|_{r_s}^R \\ = - \int_{r_s}^R \left[\frac{2}{r} + V(r) \right] U_h^{(l,n)} U^{(l,n)} dr. \quad (7)$$

Since at $r=R$,

$$U^{(l,n)} (dU_h^{(l,n)}/dr) - U_h^{(l,n)} (dU^{(l,n)}/dr) = 0,$$

we have

$$\left. \frac{r}{U^{(l,n)}} \frac{dU^{(l,n)}}{dr} \right|_{r=r_s} = \left. \frac{r}{U_h^{(l,n)}} \frac{dU_h^{(l,n)}}{dr} \right|_{r=r_s} \\ - r_s \int_{r_s}^R dr \left(\frac{2}{r} + V(r) \right) \frac{U_h^{(l,n)}(r)}{U_h^{(l,n)}(r_s)} \cdot \frac{U^{(l,n)}(r)}{U^{(l,n)}(r_s)}. \quad (8)$$

Here, $U_h^{(l,n)}(r)$ can be calculated by (1), and (8) is the equation to be solved with respect to $U^{(l,n)}(r)$. If we put $V(r) = -2Z(r)/r$. Where $Z(r)$ is the effective nuclear charge, $Z(r)$ is not much different from unity in the vicinity of r_s . The quantity

$$\Delta V(r) = -\frac{2}{r} - V(r) = \left(\frac{Z(r)}{r} - \frac{1}{r} \right) 2, \quad (9)$$

which is involved in (8), is the deviation of the true potential from the pure hydrogenic form, and is small near r_s , and vanishes for all $r > R$. Since, therefore, the integral on the righthand side of (8) is small, and $U^{(l,n)}(r)$ may not be appreciably different from $U_h^{(l,n)}(r)$, we may assume, as the first approximation, that $U^{(l,n)}(r)$ in the integrand can be replaced by $U_h^{(l,n)}(r)$. Thus, we obtain the first approximation formula for the logarithmic derivative of the true wave function:

$$\phi_l(r_s) = \left[\frac{r}{U^{(l,n)}} \frac{dU^{(l,n)}}{dr} \right]_{r=r_s} = \left[\frac{r}{U_h^{(l,n)}} \frac{dU_h^{(l,n)}}{dr} \right]_{r=r_s} \\ + r_s \int_{r_s}^R \Delta V(r) \left(\frac{U_h^{(l,n)}(r)}{U_h^{(l,n)}(r_s)} \right)^2 dr. \quad (10)$$

If we want more accurate values of $\phi_l(r)$, we may employ successive approximations. First the values of ϕ_l are calculated by (10) at several values of r . For large values of r , $r > R$, $U^{(l,n)}(r)$ should be equal to the uncorrected $U_h^{(l,n)}(r)$ which can be obtained by (1). Then, we integrate $\phi_l(r)$ numerically, starting at a large value of r toward smaller values of r . The values of $U^{(l,n)}(r)$ thus obtained will give a better approximation to the true values of $U^{(l,n)}(r)$, and will be used in computing the integral on the righthand side of (8). In this way, one obtains the second approximation to the logarithmic derivative ϕ_l . This procedure can be repeated until we get the self-consistent solution of (8).

3. COHESIVE ENERGY OF THE NOBLE METALS

The method developed in the preceding section will be applied to the calculation of the cohesive energy of the monovalent noble metals, *viz.*, copper, silver, and gold.

The uncorrected wave function $U_h^{(l,n)}(r)$ is calculated by (1). The confluent hypergeometric functions involved are evaluated from the tables calculated by Ham⁸ who has revised and extended the tables published by Kuhn.⁹ In calculating k_l for the uncorrected s -function, the extrapolation of δ_0 from the free-atom term values listed by Bacher and Goudsmit¹⁰ is employed for all three metals.

In the case of p -levels, however, the information from the free atom term values is not sufficient for determining the dependence of the quantity η_1 defined by (3) upon the energy parameter ϵ . Moreover, the term values of the p -series of copper show marked irregularity which is attributed to configuration interactions. Whitelaw¹¹ has given a theory which permits the estimation of the unperturbed positions of the p -series. The unperturbed positions of the $4p$ and $6p$ term assigned by Whitelaw and the energy parameter of the Hartree-Fock equation for the $3p$ electron¹² are used in deriving the $\eta_1 - \epsilon$ relation for copper. The $5p$ term is not used because the influence of the other perturbing multiplet on this term seems to be appreciable and is not properly incorporated in the treatment of Whitelaw. For silver and gold, the x-ray term values together with the spectroscopic term values are used in deriving the relation. Thus η_1 is expressed as a function of ϵ for all three metals, and from η_1 we can calculate k_l involved in the calculation of p -functions by (1).

We now apply Eq. (10) to the evaluation of the logarithmic derivatives, if ΔV is known. For copper, the values of the effective nuclear charge $Z(r)$ calculated by the Hartree-Fock method are available.¹² For silver and gold, $Z(r)$ will be extrapolated from that of copper as follows. As we shall see later, the lattice spacing of copper is mainly determined by the repulsive force between ion-cores when they come into contact. We shall call this repulsion the ion-core repulsion hereafter. Now, we may assume that the size of the ion core determines the lattice spacing of silver and gold as well. Therefore, by comparing the observed lattice constants of silver and gold with that of copper, we can estimate the form of the ion-core potential of silver and gold. The Hartree-Fock values of $\Delta V(r)$ for copper can be approximated by means of the analytical expression

$$\Delta V(r) = \beta r^{-1} \exp -\alpha_1 r \quad \text{for } 1.4 \bar{z} r \bar{z} 3.4, \quad (11)$$

$$= 0 \quad \text{for } r \bar{z} 3.4,$$

⁸ F. Ham (private communication).

⁹ T. S. Kuhn, *Quarterly of Appl. Math.* **9**, 1 (1951).

¹⁰ R. F. Bacher and S. A. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

¹¹ N. G. Whitelaw, *Phys. Rev.* **44**, 544 (1933).

¹² D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A157**, 490 (1936).

with

$$\alpha_1 = 2.438, \quad \beta = 27.53. \quad (12)$$

Let us assume that the form of $\Delta V(r)$ for silver as well as for gold is analogous to (11), and also that the values of β and ΔV at r corresponding to the observed lattice spacings are identical for all three metals. Then, remembering the observed lattice constant is 3.60 Å for copper, and 4.06 Å for silver and gold, we find that $\alpha_1 = 2.113$ for silver and gold. The radius R , outside of which ΔV vanishes, is assumed to be proportional to the observed lattice constants, and we have $R = 3.4$ for copper and $R = 3.8$ for silver and gold. Thus the form of ΔV for silver as well as gold is determined.

The logarithmic derivatives $\phi_0(r_s)$ of s -functions are computed by (10) for several s -sphere radii, and the values of ϵ_0 which satisfy the boundary condition $\phi_0(r_s) = 1$ are determined as the ground state energy. The logarithmic derivatives $\phi_1(r_s)$ of p -functions are also calculated by (10), where the energy parameter is taken to be equal to ϵ_0 . The Fermi energy ϵ_F is evaluated by the well-known formula¹³

$$\epsilon_F = 2.21 \alpha r_s^{-2}, \quad (13)$$

$$\text{where} \quad \alpha = \gamma [\phi_1(r_s) - 1]. \quad (14)$$

$$\gamma = -\frac{1}{3} r_s^2 (\partial \phi_0(r_s) / \partial \epsilon_0)^{-1}. \quad (15)$$

Finally, Coulomb, exchange, and correlation energies are approximated by means of the expression

$$\epsilon_C = 0.284 r_s^{-1} - 0.576 / (r_s + 5.1) \quad (16)$$

given by Wigner.¹⁴

In the case of copper, we carried out the successive approximations until we obtained the self-consistent solution of (8), but we found that the accuracy of (10) was sufficiently good for our purpose. Therefore, the logarithmic derivatives involved in the calculation of ϵ_0 and ϵ_F are evaluated by (10).

The results of our calculation are summarized in Table I. The cohesive energy ϵ_{coh} in this table may be regarded as the cohesive energy resulting from the valence electrons. The lattice structure of the monovalent noble metals is face centered cubic. The lattice constant is 3.60 Å for copper and 4.06 Å for silver and gold. The corresponding sphere radius is 2.66 for copper, and 2.99 for silver and gold, all in Bohr units. We readily see from Table I that the cohesive energy due to the valence electrons does not have a maximum at the observed lattice spacing for any of these metals. This means that the ion-core repulsion is of importance in realizing the maximum of the cohesive energy at the observed lattice spacing.

Fuchs⁴ has estimated the ion-core repulsion energy of copper by a modified Thomas-Fermi method. He has

¹³ J. Bardeen, *J. Chem. Phys.* **6**, 367 (1938); R. A. Silverman, *Phys. Rev.* **85**, 227 (1952); W. Kohn, *Phys. Rev.* **87**, 472 (1952).

¹⁴ E. P. Wigner, *Phys. Rev.* **46**, 1002 (1934); *Trans. Faraday Soc.* **34**, 678 (1938).

TABLE I. The calculation of the energy of valence electrons. ϵ_{coh} is the difference between the binding energy $\epsilon_0 + \epsilon_F + \epsilon_C$ and the first ionization potential. α and γ are defined by Eqs. (14) and (15) respectively. z_s is equal to $(8r_s)^{1/2}$. The values in brackets are those obtained by assuming a pure hydrogenic potential, in which case $\Delta V = 0$.

Metal	z_s	ϵ_0	γ	α	ϵ_F	ϵ_{coh}
Copper	4.0	-1.406 Ry (-1.508)	1.189 (1.264)	0.933 (0.918)	0.515 Ry (0.507)	0.262 Ry (0.372)
	4.5	-1.147 (-1.158)	1.034 (1.046)	0.983 (0.983)	0.339 (0.339)	0.203 (0.214)
	5.0	-0.952 (-0.953)	0.891 (0.893)	0.987 (0.988)	0.223 (0.224)	0.140 (0.140)
Silver	4.5	-1.175 (-1.210)	1.096 (1.124)	0.988 (0.949)	0.333 (0.327)	0.248 (0.289)
	5.0	-0.967 (-0.971)	0.929 (0.934)	1.010 (1.006)	0.229 (0.228)	0.160 (0.165)
	5.5	-0.819 (-0.819)	0.789 (0.789)	1.003 (1.003)	0.155 (0.155)	0.097 (0.097)
Gold	4.5	-1.293 (-1.321)	0.897 (0.916)	0.984 (0.861)	0.339 (0.297)	0.239 (0.309)
	5.0	-1.062 (-1.066)	0.781 (0.786)	1.006 (1.004)	0.228 (0.227)	0.135 (0.140)
	5.5	-0.903 (-0.903)	0.639 (0.639)	0.969 (0.969)	0.150 (0.150)	0.065 (0.065)

shown that the ion-core repulsion begins to be appreciable at an interatomic distance of 5.5 a.u., which corresponds to $r_s = 3.03$ or $z_s = 4.93$, and it increases very rapidly as the interatomic distance decreases. This means that the ion-core is almost rigid. Combining values of ϵ_{coh} given in Table I with the ion-core repulsion energy given by Fuchs, we find that the equilibrium lattice constant is 4.2 Å, and the total cohesive energy is 1.89 eV (43.5 kcal/mole) for copper. The observed values for these constants are 3.6 Å and 3.52 eV, while the values obtained by Fuchs are 4.2 Å and 1.45 eV. From the comparison of the calculated and observed values of lattice constant, one can conclude that the ion-core repulsion estimated by Fuchs starts to rise at too large an interatomic distance. In the present paper, however, we will not try to improve the calculation of the ion-core repulsion. Instead, we shall make use of the fact that the ion core is almost rigid. If we assume that the ion cores of the noble metals are rigid spheres, the interatomic distances are determined by the ion-core radii, while the total cohesive energies are equal to the cohesive energies due to the valence electrons. We calculate the radii of the s -spheres from the observed lattice constants for these metals, and determine the cohesive energy at those radii by interpolating values of

ϵ_{coh} given in Table I. Since the ion-core repulsion contributes very little to the total cohesive energy, as is shown for copper by Fuchs, the cohesive energy due to the valence electrons calculated at the observed lattice spacings should be a good approximation to the total cohesive energy. The results are given in Table II, where values of α at the observed lattice spacings are included as well.

CONCLUSION

The agreement with the observed values of the cohesive energy is fairly good for copper and silver, but not so good for gold. We shall point out some of the shortcomings in the present calculation: (I) The calculation of the uncorrected p -function is relatively inaccurate, because the information from the spectroscopic term value on the dependence of η_1 on ϵ is insufficient. In the case of copper, the configuration interaction aggravates the situation. (II) The ion-core potentials for silver and gold are extrapolated from that of copper. Although the corrections due to ΔV are small, the errors in ΔV may have introduced small errors in the final results. (III) The ion-core repulsions are not treated accurately. In fact, we have assumed the rigidity of the ion-core, and neglected the contributions from the repulsive energy to the cohesive energy. (IV) We have neglected terms with powers higher than the second in the expansion of the energy into the power series of k .

TABLE II. The calculated and observed values of cohesive energy and the calculated values of α . The theoretical values are calculated at the observed lattice spacings.

Metal	Cohesive energy in kcal/mole			α	
	Corrected ^a	Uncorrected ^b	Observed	Corrected ^a	Uncorrected ^b
Copper	59.3	59.9	81.2	0.988	0.989
Silver	55.8	58.9	68.0	1.008	0.985
Gold	48.9	53.3	92.0	1.006	0.987

^a Calculated with corrections due to the deviation of the effective ion-core potential from the pure hydrogenic form.

^b Calculated by assuming a pure hydrogenic potential.

The fourth-power term may contribute appreciably to the Fermi energy.

Finally the values of α listed in Table II are the reciprocal values of the ratios of the effective electron mass to the free electron mass. Hence, the effective electron mass calculated near the bottom of the lowest Brillouin zone is almost equal to the free electron mass for all three noble metals.

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