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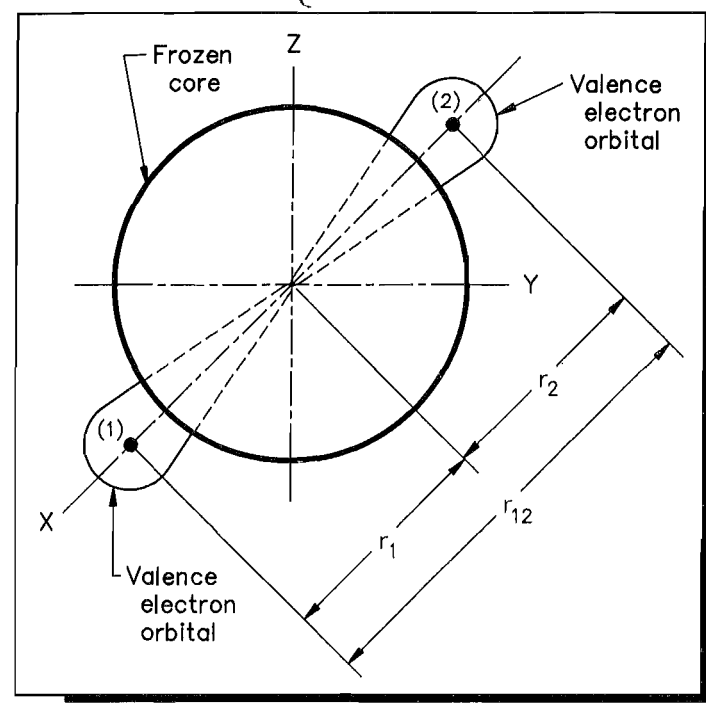
Calculation of Promotion Energies and Atomic Sizes for Atoms With Two Valence "S" Electrons: Supplement to Engel-Brewer Theory for Alloy Design

By Jack R. Woodyard

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**Calculation of Promotion Energies and Atomic
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**UNITED STATES DEPARTMENT OF THE INTERIOR
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BUREAU OF MINES

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CALCULATION OF PROMOTION ENERGIES AND ATOMIC SIZES FOR ATOMS WITH TWO VALENCE "S" ELECTRONS: SUPPLEMENT TO ENGEL-BREWER THEORY FOR ALLOY DESIGN

By Jack R. Woodyard¹

ABSTRACT

Bonding angles, promotion energies, and relative atomic sizes can be estimated through the solution of a set of algebraic equations generated from simple atomic models, and quantum mechanical parameters such as bond strength can be estimated from simple, hydrogenic form-wave functions. The precepts of The Engel-Brewer Theory are melded with the "Crystal Approximation Model" to produce atomic-structure models making these predictions. The two-valence-electron case is presented in this report. For the candidate atoms Be, Mg, Ca, Sr, and Ba the calculated promotion energies agreed within a few percent of their experimental values. These atomic parameters determine the possible crystal structure of the candidate atoms when alloyed. This is part of the effort at the U.S. Bureau of Mines to develop methods for alloy design in response to requirements for new high-performance alloys that conserve critical or rare materials.

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INTRODUCTION

Many new high-performance alloys, particularly intermetallics, show promise in novel applications or as replacements for stainless steels or other alloys containing Cr, Ni, Co, and Mg. Alloy design has been largely empirical because of the lack of thermodynamic data, good models, and a solid theoretical background. Attempts to remedy this situation include exacting quantum mechanical treatments (1),² large thermodynamic computer programs (2), or the Engel-Brewer Theory (EBT) (3), the latter being an attempt to roughly predict possible phases in multicomponent systems. Scientists at the USBM are developing new models for alloy design and applying these models to predict the crystal structures of iron aluminide based ternary compounds. This research is part of the USBM's mission to ensure an adequate supply of important minerals and materials.

The EBT estimates the maximum possible number of crystal structures (restricted to those for which the Engel correlation has been made; bcc, hcp, fcc, σ , P, μ , R, η , and diamond cubic) for an alloy or element. Other factors

that may influence the number are relative atomic sizes, promotion energies (the energy required to "promote" the atom from its vapor ground state to the electronic configuration exhibited in the solid), and electron suppression. Intermediate crystal structures, e.g., orthorhombic, are ignored, but the physical properties of many alloys can be estimated closely enough to guide experimental alloy design.

The "Crystal Approximation Model" (CA) is defined by restricting the electronic structure of an atom to electrons that are "as far apart as possible (4)." The CA gives reasonable values for atomic energies, but it is cumbersome for cases involving more than a few electrons. Adding some EBT postulates to the CA remedies this situation and allows for the useful prediction of several atomic parameters. The simplest case, i.e., for two valence electrons, predicts promotion energies well and predicts bonding angles compatible with those reached using the molecular orbital method (5).

ACKNOWLEDGMENTS

The author would like to thank Phillip Altick, professor of physics, University of Nevada, Reno, for reviewing many quantum mechanical concepts, and for helping to eliminate

the blind alleys in the author's efforts to expand the CA to this application.

THEORY

There have been many attempts to approximate atomic structure by reducing it to a superposition of hydrogen-like states (6). Usually, each electron is pictured as having a screened nuclear potential that is accounted for in the wave functions by use of a screening constant or screening term. An alternate approach is to modify the principal quantum number in a similar fashion. The CA uses the former method to estimate atomic energy levels. As a product of the form of the CA approach, potential bonding angles are estimated as well. With a combination of both the screened charge and modified quantum number techniques, and reference to certain postulates of the EBT, accuracy is improved so that promotion energies and

relative atomic sizes can be calculated. The premises from the EBT include the following:

(1) Electrons can not be promoted from closed shells (shells in which all possible electrons are present, e.g., 6 p electrons with the same principal quantum number). Therefore, inner, closed shells can be "frozen" using the CA.

(2) Paired electrons are nonbonding. Therefore, configurations like $n(s^2)$ are inert. For bonding to take place one electron must be promoted to provide an $n(sp)$ configuration.

(3) The alloy structure is determined solely by the s and p electrons. The presence of d and f electrons is important in bonding strength, particularly at high pressures, and they act as a supply or sink of electrons to be

²Italic numbers in parentheses refer to items in the list of references at the end of this report.

promoted to, or suppressed from, bonding s or p orbitals. (The d and f orbitals generally are retracted into the core.)

The Hamiltonian operator, measured in Hartree units, is determined by

$$H = \sum_{i=1}^2 \left[-\frac{1}{2} \Delta_i - \frac{Z_i}{r_i} \right] + \frac{1}{r_{12}}, \quad (1)$$

where H = Hamiltonian operator, Hartree units,

Δ_i = Laplacian operator,

Z_i = effective nuclear charge,

r_1 = radius of electron orbit₁,

r_2 = radius of electron orbit₂,

and $r_{12} = r_1 + r_2$ (see figure 1).

(Hartree units are defined to minimize the number of fundamental constants to be carried along in the algebra of the Schrödinger equation; equation 2. The unit of energy is twice the Rydberg unit so that 1 Hartree of energy equals 2×109737.3 centimeters⁻¹ $\approx 2 \times 1.312779 \times 10^6$ joules/mol (6).)

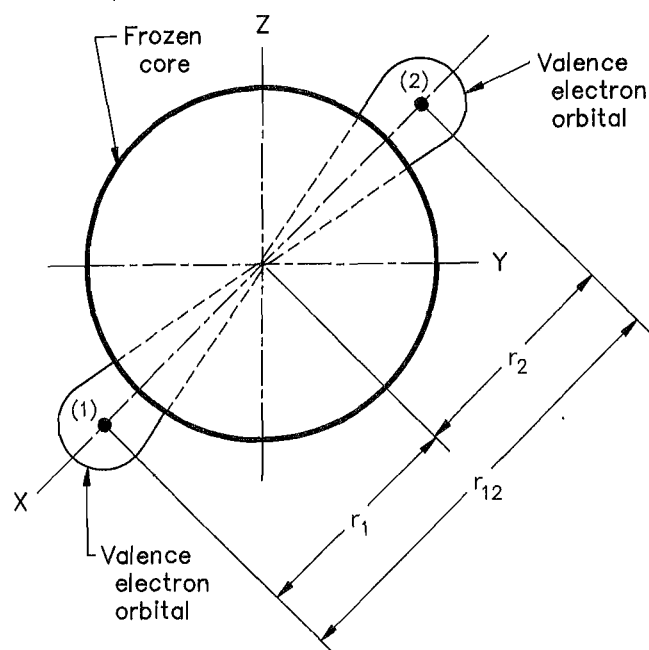


Figure 1.—Modified CA orbitals for an atom with frozen core and two valence electrons.

The Schrödinger equation for a two-electron case with the frozen core ignored can be written

$$H\Psi = E\Psi, \quad (2)$$

where E = eigenenergy,

and Ψ = complete product from wave-form function for two electrons.

By symmetry

$$\frac{1}{r_{12}} = \frac{1}{2(1+a)r_1} + \frac{a}{2(1+a)r_2}, \quad (3)$$

where $a = \frac{r_2}{r_1}$.

When equations 1 and 3 are substituted into equation 2 the wave equation can be separated into the product of two hydrogenic-wave equations with each electron having a screened nuclear charge:

$$Z_1 = Z - \frac{1}{1+a}, \quad (4)$$

and
$$Z_2 = Z - \frac{a}{1+a}, \quad (5)$$

where Z_1 = effective nuclear charge of electron₁,

and Z_2 = effective nuclear charge of electron₂.

Because of the frozen core, $Z = 2$. Note the asymmetry in the form of the two screened charges, Z_1 and Z_2 . This asymmetry is counter to normal quantum mechanical precepts of indistinguishable particles and is a direct result of using a as the ratio of the radii. The limits as one electron is removed to infinity do not pass to the value for a one-electron atom of nuclear charge Z , so this approximation is only operable when lower lying atomic states are considered. (As the "outer" electron is moved to infinity, i.e., the atom is ionized, the outer electron will have a charge of $Z-1$, but the "inner" electron will have no screening; equation 4 predicts the outer electron having a charge of $Z-1/2$.)

A core (i.e., multi-electron environment) will influence the energy-level spacing sufficiently so that promotion energies calculated from these equations will contain large errors.

Using the hydrogenic form of the expectation value of the radius, a is determined. From the expectation value of

a, Z_1 , and Z_2 are determined. The number β is found by fitting the resulting equation to empirical values of E using

$$\beta = n - \sqrt{\frac{Z_1^2 + Z_2^2}{-2E}}, \quad (6)$$

where β = principal quantum number correction parameter,³

and n = principal quantum number for the outer shell.

The resulting values of β are fit by regression analysis to determine β as a function of n . Tables 1 and 2 show examples of calculating the values of β for candidate atoms Be, Mg, Ca, Sr, and Ba.

Table 1.— β values from equation 8, empirical values of ground state energies, and number n^* calculated from equation 7 in Hartree units

Element	Electron configuration	n	E^1	β	n^*
Be	2s ²	2	-1.012	0.2601	1.7399
Mg	2s ²	3	-.833	1.0829	1.9171
Ca	4s ²	4	-.661	1.8472	2.1528
Sr	5s ²	5	-.614	2.7675	2.2325
Ba	6s ²	6	-.559	3.6594	2.3406

¹Ground state.

RESULTS AND DISCUSSION

Because of the complex, multibody nature of the atomic system, β would be expected to exhibit a complex relationship to the principal quantum number, effective nuclear charge, and other parameters associated with the atomic system. A significant result of the application of the EBT to the CA was that the parameter β fit the empirical data linearly. With a slight modification, where two groups were used (group 1—Be, Mg, and Ca; and group 2—Ca, Sr, and Ba), the fit was excellent (table 3).

In figure 2 the calculated value of β is plotted against the principal quantum number for the outermost electrons. Experimental data are superposed as circles or squares on the calculated lines. The linearity of the β function is as

³ β is determined empirically from published energy level data (7). Physically, β is a measure of how the normal, hydrogenic orbitals are squeezed into the core by the effect of multi-electron potential superposed over the large nuclear charge, Z . Like the principal quantum number, β is a number without units.

Table 2.—Energy, β , and n^* values from regression analysis applied to model

Element	Calculated values				n^*	Error, pct ¹
	Electron configuration	n	E^2	β		
Be . .	2s ²	2	-1.023	0.2698	1.7302	-1.131
Mg . .	3s ²	3	-.817	1.0634	1.9366	2.0052
Ca . .	4s ²	4	-.667	1.857	2.143	-.913
Ca . .	4s ²	4	-.664	1.852	2.148	-.439
Sr . .	5s ²	5	-.609	2.758	2.242	.8392
Ba . .	6s ²	6	-.561	3.6641	2.3359	-.404

¹Standard error of the mean.

²Ground state.

To compensate for the errors caused by the influence of energy-level spacing use

$$n^* = n - \beta, \quad (7)$$

where n^* = effective principal quantum number.

remarkable as the fit to the experimental data for both the ground and promoted states.

Table 3.—Regression constants for determining β from experimental data

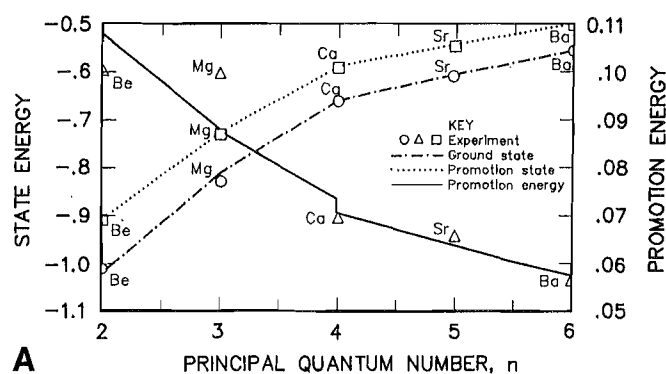
State	Group	Constant		Coefficient	
		Value	Error, pct ¹	Value	Error, pct ¹
Ground . . .	Be, Mg, and Ca	-1.32	0.024	0.794	0.017
	Ca, Sr, and Ba	-1.77	.012	.906	.008
Promoted . .	Be, Mg, and Ca	-1.39	.009	.779	.006
	Ca, Sr, and Ba	-1.89	.008	.904	.006

¹Standard error of the mean.

The energies of the valence electrons and the promotion energies (ignoring the frozen cores) were calculated using the functional dependence of β and are plotted in figure 3A. Promotion energies are calculated as the

(small) difference of two large numbers, and so they are very sensitive to any inadequacies of the model. In figure 3A the "step" at Ca is the result of using the two element groups for regression analysis. The scatter in the first group is greater than the scatter in the second group. With Be being a very light element (only 4 electrons) many of the screening effects due to a substantial core of inner electrons are not present. Even with Be in the calculation the error for the promotion energies is less than 12 pct. The absolute errors in the determination of the ground state, promoted (excited) state, and the promotion energies are depicted in figures 3B, 3C, and 3D, respectively. For each case the experimental values are plotted against the calculated values. The extremely good reproduction of the ground-state and promoted-state energies are evident in these plots, and the relatively poor conformance of the promotion energies for Be and Mg is readily apparent.

Relative atomic sizes (fig. 4A) show the expected increase in atomic radius as the atomic number increases.



A

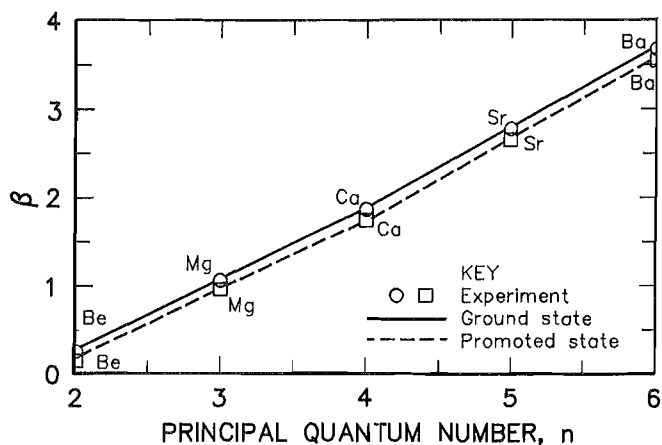
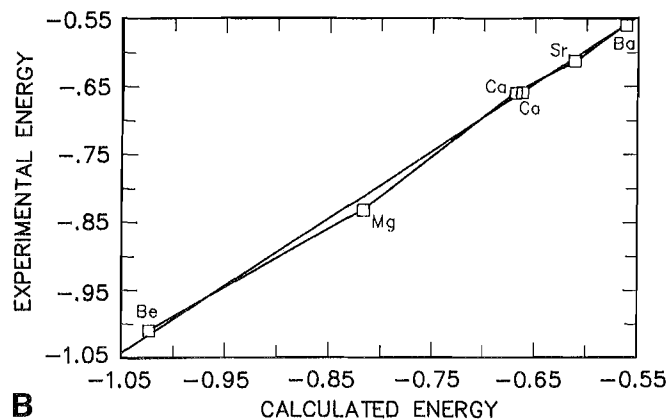
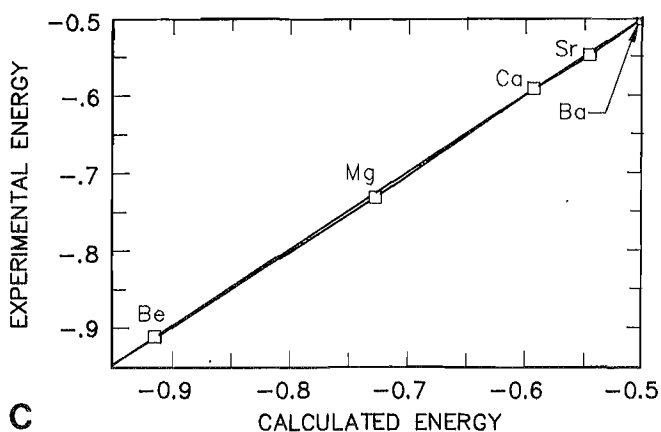


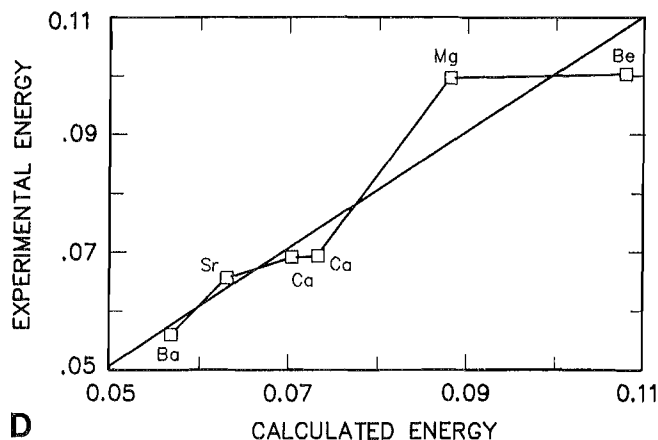
Figure 2.—The correction term β to principal quantum number n^* as calculated for the ground and promoted states from empirical data.



B



C



D

Figure 3.—State energies and promotion energies in Hartree units for two valence electrons outside of a frozen core. A, State and promotion energies as a function of principal quantum number; B, absolute error plot of the ground state energy; C, absolute error plot of the excited state energy; and D, absolute error plot of the promotion energy.

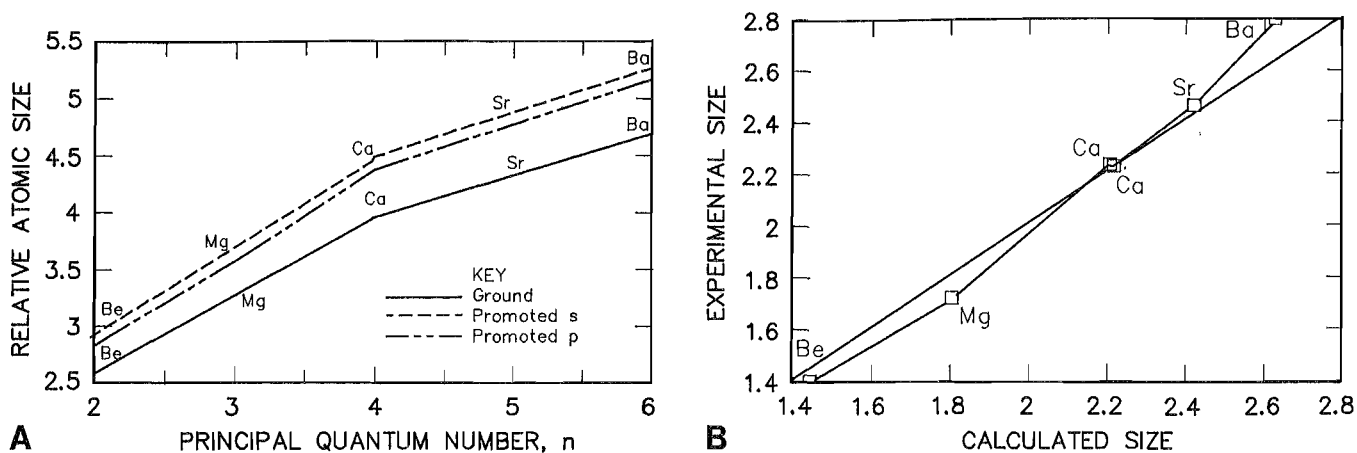


Figure 4.—Relative atomic sizes in Hartree units for the ground and promoted states. A, Relative atomic size as a function of principal quantum number; B, absolute error plot for the relative atomic sizes.

As the candidate atoms get heavier, the tendency of the relative atomic sizes to level off is seen in the change in the slope of the curves between the two groups. (The contraction of closed shells and the incomplete screening of the nuclear charge by the inner electrons is well known in atomic theory, and is the basis for the correction term, β .) The tendency of orbitals with higher angular-momentum-quantum numbers to be drawn into the core is also illustrated. A d orbital would be drawn almost completely into the core as postulated by the EBT and thus would affect the bond strength, but not the crystal structure. Figure 4B shows the absolute error plot for the predicted atomic sizes.

Bonding angles will be influenced strongly by where the electrons (and electron "holes") have their highest position-expectation values relative to those of another atom in the compound. The CA forces the electrons to be on opposite

sides of the nucleus, and agrees with the configurations of most probability for two valence electrons calculated by molecular orbital methods. In the two-valence-electron case the angle between the electrons is 180° (for example see reference 5). The two-electron case is not very interesting geometrically, but preliminary results indicate that elements with up to four valence electrons show angles between the promoted electrons that vary with increasing atomic number. Size effects should be a natural byproduct of this model.

These results are used in Slater-determinate wave functions. The elements of the Slater-determinate are screened-hydrogenic wave functions using n' , Z_1 , and Z_2 . Calculation of bonding strengths, ranges, and other quantum mechanically determined parameters can be made relatively easily, but such calculations are beyond the scope of this paper.

CONCLUSIONS

The use of the combined CA-EBT model shows potential in directly estimating bonding angles, promotion energies, relative atomic sizes, and pseudoquantum mechanical calculations of mechanical properties for various

alloys. Principal-quantum-number corrections based on empirical data show a remarkable linearity over a broad range of elements.

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