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ABSTRACT

A theoretical and experimental study was made of the shift in atomic core-electron binding energies caused by the chemical environment.

Two models are presented to account for these "chemical shifts." The first uses an energy cycle to break the core-electron binding energies into a free-ion contribution and a classical Madelung energy contribution. The Madelung energy contributes a significant part of the binding energy shift. It can in principle be evaluated rigorously, although there is some ambiguity as to a surface correction. The reference level for binding energies must also be considered in comparing theory with experiment (or in comparing experimental shifts with one another). Electronic relaxation could also introduce errors of ~1 eV in shift measurements. The second, more approximate, model consists of a "charged-shell" approximation for bonding electrons in atomic complexes. It gives semi-quantitative estimates of shifts and demonstrates the relationship between bond polarity and core-electron binding energy shifts.

These models indicate that several features of the free-ion state will be reflected also in chemical shifts. Free-ion Hartree-Fock calculations were made

on F, Cl, Br, I, and Eu in several oxidation states. These indicate that the removal of a valence electron shifts the binding energies of all core levels by nearly equal amounts (10-20 eV). This shift decreases with increasing atomic number in a given chemical family. The removal of an inner "valence" electron (e.g., 4f in europium) gives rise to relatively large shifts (~20 eV). These features were also found in the experimental chemical shifts

Chemical shifts were measured for iodine in KI, iodobenzoic acid, KIO_3, and KIO_4 and for europium in $EuAl_2$ and Eu_2O_3, using the technique of photoelectron spectroscopy. Binding energies in iodine were found to increase by ~0.8 eV per unit increase in oxidation number. A Madelung energy calculation indicates that this corresponds to a loss of ~0.5 electronic charges from the valence shell per unit increase in oxidation state, and this value agrees approximately with previous results obtained from Mössbauer measurements. A shift of 10 eV was found between Eu^{+2} and Eu^{+3}. This very large shift is due largely to the loss of a full 4f electron in this change of oxidation state.

With some refinements, the above technique could produce very useful information about bonding in ionic solids, in particular allowing the determination of the charge on each atom. Their application to such problems as a determination of the oxidation states of metals in biological molecules seems even more promising.

I. INTRODUCTION

There are two main techniques for studying the binding energies of atomic core electrons. Traditionally, x-ray emission and absorption spectroscopy have been used in this type of investigation. However, during the last ten years a photoelectron spectroscopic method has been developed to sufficient precision and accuracy that it now surpasses the x-ray techniques in many respects. A detailed description of the technique has previously been published.[1] The method is simple and direct. Photoelectrons from inner shells are expelled by x-radiation of known energy. The kinetic energy of these photoelectrons is measured in a high resolution electron spectrometer. From the photon energy and the kinetic energy the binding energy of a particular subshell is readily obtained.

Chemical effects on core-electron binding energies have been observed since about 1920 in x-ray emission and more often in x-ray absorption spectra.[2] However, experimental difficulties as well as ambiguities in the interpretation of spectra have inhibited the usefulness of conventional x-ray techniques for studying chemical effects. The photoelectron spectroscopic technique however, shows much promise in this area. For example, application of photoelectron spectroscopy to sodium thiosulfate very directly indicates that there are two distinct types of sulfur atoms present.[3] That is, the photoelectron spectrum due to the sulfur $1s_{1/2}$ shell is split into two well-resolved peaks approximately 6 eV apart, the two peaks being due to sulfur atoms in the -2 and +6 formal oxidation states. Furthermore, measurements on a series of sulfur compounds reveal a monotonic relationship between binding energy and formal oxidation state.[4] Subsequent studies have also been made on the elements carbon,[5] oxygen,[5] nitrogen,[6] and chlorine.[7]

In this paper we report photoelectron spectroscopic measurements on compounds of iodine (Z=53) and europium (Z=63). As previous work has been done primarily on light elements it was of interest to measure chemical shifts for heavier atoms. Iodine was chosen because it forms stable compounds over a wide range of oxidation states and also because its bonding has been studied with the Mössbauer effect.[8] We have studied the chemical shifts for the iodine core levels $2s_{1/2}$ to $4d_{3/2}$ in compounds with formal oxidation states ranging from -1 to +7. Europium was chosen because the 4f configurations are known to be $4f^7$ for Eu^{2+} [9] and $4f^6$ for Eu^{3+}.[10] We therefore expected a large shift between +2 and +3 compounds due to the completely "ionic" nature of the 4f transfer involved. We have studied europium in the +2 state (as $EuAl_2$ and to a lesser extent EuS and EuO) and the 3 state (as Eu_2O_3). The measured shifts for europium are large, being about 9.6 eV for this unit change in oxidation state compared to 0.8 eV for iodine.

We have also made a theoretical analysis of chemical shifts in core electron binding energies. A model was developed which makes use of the classical model for ionic crystals. To a good approximation, the binding energy of a core electron in a solid is composed of two parts: a free-ion contribution and a lattice-potential correction. Free-ion calculations were made using a self-consistent field Hartree-Fock computer program written by Roothaan and Bagus.[11] The lattice potential correction can be related to the Madelung energy of the crystal and evaluated for the iodine compounds of primary interest (KI, KIO_3, and KIO_4). Comparison of experimental and theoretical results then permits assignment of a charge to the iodine atom in each compound, or, less directly, to a determination of the "fractional ionic character" of the iodine bonds.

The instrumentation and experimental techniques are described in Sec. II. In Sec. III we discuss briefly the system of data analysis. The experimental results are presented in Sec. IV. Section V contains a general discussion of the theoretical evaluation of such chemical shifts, pointing out several corrections. We also present here the results of specific calculations on europium and iodine. In Sec. VI we discuss the experimental results in the light of our theoretical values, and also make suggestions for applying this technique to biological problems. Conclusions are given in Sec. VII.

II. INSTRUMENTATION AND EXPERIMENTAL TECHNIQUE

Photoemission from a solid may be considered as a three-step process. Electrons are excited to higher energy levels by absorption of a photon. The excited electrons move through the crystal lattice and some of them reach the surface. If their momenta perpendicular to the surface are large enough they escape into the vacuum and their kinetic energies can be measured. On their way out to the surface the photoelectrons may lose energy by various kinds of inelastic collisions. In this work we are interested primarily in those electrons that have not suffered any large, discrete energy losses of the order of several eV, the most common of which are those due to plasmon creation and interband transitions.

When studying the inner atomic energy levels we use photon energies well above the photoelectric thresholds for these levels. The kinetic energies of the photoelectrons of interest are typically in the range 1-5 keV. In order to separate out the elastically scattered electrons from those that are inelastically scattered, high-resolution electron spectroscopy is necessary. An iron-free, double-focusing magnetic spectrometer was used in this work.[12] Bergkvist[13] has doubled the transmission of this spectrometer for a given resolution by means of external correction coils. The apparatus is schematically illustrated in Fig. 1.

The momentum resolution was set to 0.03% (full width at half maximum intensity). This gives a line width in energy ranging from 0.6 eV for 1 keV electrons to 3 eV for 5 keV electrons. It is advantageous to work at low photoelectron energies to achieve both the best absolute resolution and the highest photoelectric yield.

The detector was a Geiger counter with a thin 50-75 $\mu g/cm^2$ formvar window. The window had a cut-off energy of 3-4 keV. To reduce the effective cut-off

energy a post-accelerating device was fitted between the exit slit of the spectrometer and the counter window. The electrons could thus be given an extra energy of up to 4 keV before entering the counter. The effective cut-off with the post-acceleration detector system was about 1 keV.

The data were taken by stepping the spectrometer current, usually in increments of 0.2 mA and counting for a preset time at each point, usually 12 or 30 sec. The counts were stored in a multichannel analyzer used in the multiscalar mode. Each spectrum was scanned several times and the scans were added together in order to eliminate the effect of fluctuations in the x-ray intensity. The spectrometer current stability was 2-3 parts in 10^5.

The source of radiation was a specially-made non-magnetic x-ray tube with a demountable anode. The x-ray tube was fed from a doubly rectified high voltage generator. The excitation voltages used were 30 kV for CrKα, and 35 kV for CuKα.

The only filter between x-ray anode and source was a piece of 25 micron Al foil. Therefore, the incident radiation was by no means monochromatic and the photoelectron spectrum reflected the x-ray spectrum. The strong α_1 and α_2 x-rays give rise to easily resolvable photoelectron peaks, however. The Al filter is useful in reducing background by attenuating the soft x-ray portion of the spectrum and also by preventing electrons from scattering off the anode and entering the spectrometer. It would, of course, be desirable to decrease background radiation and approach more closely a monochromatic source. For example, a bent-crystal monochromator has been used to discriminate against all but α_1 radiation in some recent photoelectron spectroscopic work.[14] The difficulty with

most monochromatization techniques however, is that the intensity of the desired radiation is severely reduced. Recently, the use of low -Z materials such as Al for an anode has proven to be very satisfactory.[4-6] The lighter elements do not have a significant splitting between the closely spaced $K\alpha_1$ and $K\alpha_2$ x-rays so a strong "monochromatic" $K\alpha$ line occurs.

The sample arrangement is similar to one described previously.[15] An extended source (10×13 mm^2) was placed immediately in front of the x-ray tube window. The distance between the focal spot of the x-ray tube and the center of the source was about 30 mm. About 5 mm in front of the sample was a 0.5 mm by 10 mm entrance slit into the spectrometer chamber. This slit acted as the effective electron source for the spectrometer. With this arrangement the actual alignment of the sample was not critical. The highest counting rates were obtained when the angle between sample plane and slit plane was about 40°.

Samples were usually prepared by grinding a compound to a fine powder and dusting this powder onto a two-sided tape backing which was firmly pressed onto one flat face of an aluminum block. This block acted as a heat sink and an electron source to replace electrons lost in photoemission. The face of the block was mounted at the optimal source angle. Chemical shifts between different samples could be measured directly by moving the source block up or down from one of three sample positions to the next via a vacuum-tight mechanical coupling.

III. DATA ANALYSIS

It is natural to define the binding energy of an electron in a free atom as the energy necessary to remove the electron from its shell to infinity. In a solid, the outer electronic levels are broadened into bands, and a potential barrier exists at the surface; it is therefore more convenient to refer the binding energies to the Fermi level (electronic chemical potential). It would seem that the work function of the sample would then enter into the photoemission equation. However, it is actually not the work function of the source but rather that of the entrance slit and vacuum tank of the spectrometer that enters. The reason for this is illustrated in Fig. 2, which shows energy vs distance near the sample. If the sample is electrically connected to the vacuum tank their Fermi levels will coincide at equilibrium. When the electrons pass through the slit (but before energy analysis) they will therefore have acquired the vacuum potential of the entrance slit material. The vacuum tank and the entrance slit are both made of aluminum. The work function of this spectrometer (ϕ_{sp}) has been reported as 3.7±0.3 eV [16] and has been found to be stable with time. This value was used in our investigation in determining absolute binding energies. Since this correction is a spectrometer constant it will not enter into chemical shift measurements in any way.

The photoemission equation for the ith core level of an atom A in compound X will thus be

$$h\nu = E_b^f(A, i, X) + E_{kin} + \phi_{sp} \qquad (1)$$

where the binding energy $E_b^f(A, i, X)$ is referred to the Fermi level of the source. The notation E_b^V will be used later when referring a binding energy to the vacuum level of the sample. The measured final kinetic energy of the photoelectrons is denoted E_{kin}.

Absolute binding energies can thus be determined if $h\nu$ and E_{kin} are known. The energies for $CuK\alpha_1$ and $CrK\alpha_1$ have been taken from the recent tabulation of x-ray wavelengths by Bearden[17] and are 8047.78 eV and 5414.72 eV, respectively. The spectrometer was calibrated for each new sample by means of a magnesium oxide sample giving rise to the Mg $1S_{1/2}(CuK\alpha_1)$ and Mg $1S_{1/2}(CrK\alpha_1)$ photoelectron lines. The magnetic rigidities of these lines are 277.719 G-cm and 216.495 G-cm, respectively.[19] All data are based on the 1963 set of fundamental constants.

Equation 1 is exact for a metallic sample. For a semiconductor or an insulator the situation is more complicated and a certain ambiguity exists in the reference level. For such materials the Fermi level is located somewhere between the valence and conduction bands as shown in Fig. 2, i.e., in a forbidden energy gap. Therefore it does not have the simple physical meaning of the highest occupied level as in a metal. Since the portion of the sample effective in producing inelastically scattered photoelectrons is a thin layer near the surface, the situation may be further complicated by surface band-bending effects for these materials. At the moment there is not sufficient experimental evidence to solve unambiguously the question of the reference level for such materials. From the reproducibility of our experimental data, however, we conclude that for these materials the reference level remains fixed within 1 eV and tentatively we

assume that also for semiconductors and insulators the Fermi level serves as the reference level. We discuss this problem further in Sec. V.

Also one might expect that the use of insulating samples would be impossible due to inevitable charging-up effects. These have been observed, e.g., in beta-ray spectroscopy, where shifts as high as several keV have been reported. A slight charging-up effect in our work cannot at the moment be excluded. However, the effect is probably less than 1 eV.

Figure 3 shows some typical photoelectron lines from iodine compounds. The notation $I2p_{3/2}$ - $KI(CuK\alpha_1)$ denotes a peak due to electrons expelled by $CuK\alpha_1$ radiation from the iodine $2p_{3/2}$ level in a potassium iodine sample. Although all of the samples were thicker than the mean free path for inelastic collisions of the excited electrons, the photoelectron lines are well-separated from the discrete energy loss spectrum. The first energy loss peak falls 5-20 eV from the elastic peak and can thus be easily distinguished. In the case of $CrK\alpha$ excitation radiation the proximity of $CrK\alpha_1$ and $CrK\alpha_2$ (9.21 eV) influences the low energy side of the photoelectron line from $CrK\alpha_1$. However, resolution was still good enough to locate the $CrK\alpha_1$ photoelectron peak accurately.

The linewidth of a photoelectron line is typically 5 eV. Part of this is due to spectrometer broadening and part to lifetime broadening from both the sample energy level and the exciting radiation. The width contributed by the radiation is 2.26 eV for $CuK\alpha_1$ and 1.95 eV for $CrK\alpha_1$.[18] Peak locations were determined in two ways: by hand as the intersection of the locus of midpoints of horizontal chords and the photoelectron line or by a least squares computer fit of Gaussian functions to the data.

IV. CHEMICAL SHIFT MEASUREMENTS ON IODINE AND EUROPIUM COMPOUNDS

A. Iodine Compounds

Binding energy shifts were measured for eight iodine levels from $2s_{1/2}(E_b^f = 5191.6$ eV) to $4d_{5/2}(E_b^f = 54.4$ eV) in compounds of 99.9% purity, ranging from -1 to +7 in nominal oxidation state. Table I lists the levels, compounds, number of measurements, and shifts relative to KI. The scatter of individual measurements is somewhat larger than that obtained previously on metal samples. This could arise from a charging-up effect or from changes in the reference level from sample to sample, as the Fermi level of a surface layer of semiconductor or insulator could be very sensitive to both bulk impurities and surface conditions. Such fluctuations are of the order of 1 eV or less, however, and would not obscure the larger chemical shifts in KIO_3 and KIO_4. The standard deviation of these shifts due to scatter of individual measurements is quoted as an error figure. The shift is essentially the same for all the measured levels. Weighted average shifts were calculated for the core levels of each compound. For the three compounds these were: potassium p-iodo benzoate (KIBA)-0.0 ± 0.6 eV, KIO_3-5.3 ± 0.6 eV, and KIO_4-6.3 ± 0.6 eV relative to KI. Typical photoelectron lines from two iodine compounds are shown in Fig. 3. The shift in energy is obvious.

Absolute binding energies obtained from KI samples are listed in Table II. The work function correction has been applied and the binding energies therefore all refer to the Fermi level of the sample.

As the iodine compounds under investigation all contained potassium, it was of interest to measure the shift of potassium core levels also. This was

done for the $1s_{1/2}$ level in the three inorganic compounds and the shifts obtained from 5 measurements on each compound are: KIO_3 - -1.3 ± 0.2 eV and KIO_4 - -1.3 ± 0.2 eV, again relative to KI.

B. Europium Compounds

Binding energy shifts were measured for the $3d_{5/2}$ level and to a lesser extent the $3d_{3/2}$ and $4p_{3/2}$ levels of europium in the +2 and +3 oxidation states. Low intensities prevented measurements on more levels. Most of the measurements on the +2 state were made on $EuAl_2$, although preliminary data on EuS and EuO show similar shifts. The +3 state was represented by the compound Eu_2O_3. Results are presented in Table III. The weighted average shift for these measurements is 9.6 ± 0.6 eV.

Figure 4 compares photoelectron peaks from different europium compounds. Spectra B and C were obtained from a piece of europium metal which was polished in air to give a shiny surface. Spectrum B was obtained as quickly as possible after insertion into the spectrometer vacuum. Spectrum C was obtained after several days exposure of the same sample to air. The rapid oxidation of europium metal can be followed from EuO to Eu_2O_3 by the disappearance of the $3d_{5/2}$ photoelectron peak associated with Eu^{+2}. The spectrum observed is complicated by the $K\alpha_2$ photoelectron lines and perhaps discrete energy loss peaks but the interpretation is straightforward. There also appears to be some oxidation of the surface of $EuAl_2$ to the +3 state. This is further verified by the fact that the +2 peak was much weaker in older $EuAl_2$ samples, particularly those which were exposed to air.

V. THEORETICAL

A. General Procedure

In order to calculate electron binding energies in a solid compound, we must first select a reference level for energy. As discussed in Sec. III the Fermi level is suggested by our experimental method. However, for non-metals the Fermi level cannot be easily obtained theoretically, as a knowledge of the density of states of the electronic bands is required. This in turn requires a detailed quantum-mechanical treatment of every solid under study which is not feasible at the present time. We therefore select as our reference the vacuum level and define it as the energy at which an electron can escape from the surface of the solid and arrive at infinity. Our simple theory has this reference level built in, because it uses free-ion Hartree-Fock calculations.

It is also possible to suggest a method for measuring these vacuum-referenced binding energies directly. From Fig. 2 we note that all photoelectrons leaving the sample are accelerated or retarded by the difference in vacuum levels between sample and spectrometer before their kinetic energies are measured. This difference is the contact potential ϕ_c: its measurement would give a direct determination of the vacuum-referenced binding energy of an arbitrary i^{th} inner level of atom A in a solid compound X from

$$E_b^V(A,i,X) = E_b^f(A,i,X) + \phi_{sp} - \phi_c \qquad (2)$$

A chemical shift of the level i between compounds X and Y then becomes

$$\Delta E_b^V(A,i,X\text{-}Y) = \Delta E_b^f(A,i,X\text{-}Y) - \Delta\phi_c \qquad (3)$$

since ϕ_{sp} is constant. Assuming that $\Delta E_b^V(A,i,X\text{-}Y) \approx \Delta E_b^f(A,i,X\text{-}Y)$ is thus equivalent to assuming $\phi_{cx} \approx \phi_{cy}$. No contact potential measurements have been made in conjunction with photoelectron spectroscopy. However, it has been shown in previous work[3-7] and in our own measurements that the chemical state of the atom is far more important than effects of this type. As an example, we have found iodine binding energies to agree very well (±0.4 eV) between KIO_3, HIO_3 and I_2O_5, all compounds in which iodine has a nominal oxidation number of +5, but where contact potential differences might be expected. Therefore, we tentatively neglect $\Delta\phi_c$ and directly compare ΔE_b^V (theoretical) to ΔE_b^f (experimental) in Sec. VI.

Let us consider one procedure for calculating vacuum-referenced core electron binding energies and chemical shifts in solid compounds with partial ionic character and long-range order.[20] This procedure is a generalized and slightly modified version of one used previously for determining valence band locations in the alkali halides.[21] With the aid of the energy cycle shown in Fig. 5, the problem can be broken up into parts amenable to solution by relatively simple techniques. The cycle is as follows: suppose we are interested in the binding energy of a core electron in the ith level of atom (or ion) A in some solid compound X. All atoms in the lattice are assigned charges, subject to the restriction of overall electroneutrality. For strictly ionic compounds,

these charges will have integral values, whereas for other compounds their values can be empirically assigned as we demonstrate below. We first remove A from the solid lattice with whatever charge it has in the lattice (Z). All nuclei remaining in the lattice are held fixed in their equilibrium positions during the entire cycle, but the electrons can be allowed to relax about all nuclei including the one removed. E_1 is the energy required for the first step. Next, we remove a core electron from the ith level of A^Z to form A^{Z+1}. The energy required is the binding energy of the ith level of the free ion with charge Z and is denoted by $E_b^V(A,i,Z)$. Finally, A^{Z+1} is inserted back into the lattice. The energy required is E_2. If nuclear and electronic relaxation have been treated properly, the net effect of the cycle is to remove an electron from a core level. $E_b^V(A,i,X)$ is thus the binding energy in the solid referred to the vacuum level, and is given by

$$E_b^V(A,i,X) = E_b^V(A,i,Z) + E_1 + E_2 \quad . \tag{4}$$

If we now consider A in the compounds X and Y (possessing charges Z and Z', respectively) the chemical shift of the ith level of A is

$$\Delta E_b^V(A,i,X-Y) = E_b^V(A,i,Z) + (E_1)_x + (E_2)_x - E_b^V(A,i,Z') - (E_1)_y - (E_2)_y \tag{5}$$

or

$$\Delta E_b^V(A,i,X-Y) = \Delta E_b^V(A,i,Z-Z') + \Delta(E_1+E_2) \tag{6}$$

Our sign convention requires that a positive $\Delta E_b^V(A,i,X-Y)$ corresponds to tighter binding of the ith electron in compound X than in compound Y.

The assumptions concerning nuclear and electronic relaxation deserve further discussion. Since the photoelectric process is believed to occur in a time interval of the order of 10^{-18} sec,[22] whereas nuclear relaxation times are of the order of 10^{-13} sec, it is probably quite valid to hold the nuclei fixed. The question of how much the electrons relax cannot be answered unambiguously, however. The hole created in the core will have a lifetime of approximately 10^{-16} sec.[22] If the effective distance for generation of unscattered electrons extends a few hundred Angstroms in from the surface as experimental results on Al and Be indicate,[23] an electron of typical kinetic energy for our experiments (5 keV) will require up to 10^{-16} sec to escape from the surface. The time required to polarize electron clouds with no discrete changes of state is of the same order of magnitude. Therefore, even if we neglect the movement of the hole (since it would produce a large discrete shift in the photoelectron energy), electronic polarization will still occur around this hole to some unknown degree. Such polarizations would alter all three energies in our cycle. The potential magnitude of these corrections will be discussed below. We now consider each of the terms in Eq. (4) in detail.

B. Free Ion Calculations

$E_b^V(A,i,Z)$ can be calculated with existing computer programs for integral Z. As a first approximation the values of binding energy changes predicted by such calculations can be compared directly to experimental shifts. A previous theoretical analysis of chemical shifts has been done in this fashion.[24] In this work, Lindgren used a modified Hartree-Fock-Slater program to obtain binding energies for different ionic states of sulfur in the range -2 to +6. Then, by drawing a smooth curve through the $\Delta E_b^V(A,i,Z)$ points at integral charge values, the experimental $\Delta E_b^f(A,i,X\text{-pure sulfur})$ values could be made to correspond to an effective non integral charge C. It was found that C is related to the oxidation state (v) of the sulfur atom by

$$C = 0.08\ v \tag{7}$$

Using this relationship shifts could be predicted reasonably well (±1.0 eV out of about 5.0 eV) for the $1s_{1/2}$, $2s_{1/2}$, and $2p_{1/2}$ levels of sulfur in three compounds from -2 to +6 in v. However the neglect of $\Delta(E_1+E_2)$ implicit in such a treatment makes its quantitative applicability doubtful. Also, the empirical nature of C gives little detailed information about chemical bonding in the solid. We show below that C is <u>not</u> the fractional ionic character of the bond.

Our free-ion calculations were made using a computer program developed by Roothaan and Bagus.[11] This program has been used extensively in previous atomic computations and Clementi[25] has published a thorough tabulation of very

accurate wavefunctions calculated with it. These functions run only up to Z = 36 however, so that both iodine (Z = 53) and europium (Z = 63) had to be done for our work. The computational procedure is described in detail elsewhere[11]; we give only its salient features here along with the specifics of our calculation. Each atomic orbital is expanded in terms of Slater-type functions with variable orbital exponents. Hartree-Fock equations are then solved for the set of orbitals until a self-consistent field is obtained. The orbital exponents are then varied in a systematic way to minimize total energy. No approximation is used for the exchange interaction. One open shell of each symmetry (s, p, d, f) is allowed. No relativistic corrections are made. The calculations to date were all made using a basis set with one function for each symmetry 1s, 2s, etc., the only exception being the 4f shell which requires at least 2 basis functions for reasonable representation. Although addition of more functions would undoubtedly improve total energies and wavefunctions, the binding energies for the inner levels should be accurate enough to give quite good estimates of changes from one ionic state to another. In fact, comparison of some minimal basis set calculations on fluorine, chlorine, and bromine with the accurate values of Clementi showed errors of only about 5% in corresponding values for shifts in binding energy upon going from one ionic state to another. All calculations were run at least twice, once to get first estimates of orbital exponents and eigenvectors and again with these estimates as initial guesses to insure optimization. Of minor importance is the open shell coupling, which we always selected to be consistent with Hund's Rules.

The binding energies reported here are the Hartree-Fock eigenvalues and are therefore accurate by Koopmans' Theorem[26] provided that electronic

relaxation about the positive hole is not appreciable. Lindgren[27] has discussed this recently and finds changes of a few eV in the binding energies in copper when the calculations are made by taking the difference of total energies for the atom and ion. We have made calculations of this type for some levels in the fluoride and iodide ions. These are summarized in Table IV. It can be seen that core level binding energies are lower by about 4% in fluorine and only 1% in iodine when calculated by the more correct difference method. Since we are primarily interested in $\Delta E_b^V(A,i,Z-Z')$ which is a difference of two free ion binding energies and is of the order of 10 eV, a 1% correction of both binding energies in the same direction introduces only an error of 0.1 eV. Relativistic corrections will also cancel to a very good approximation in $\Delta E_b^V(A,i,Z-Z')$, not because they are necessarily small for all core levels but because they will be nearly the same for both $E_b^V(A,i,Z)$ and $E_b^V(A,i,Z')$[28] and will tend to cancel in the difference.

Calculations were made for various integral charge states of fluorine, chlorine, bromine, iodine, and europium. Fluorine and chlorine were done for comparison to the results of Clementi. Br^{+2} was done to complete the halogens since Clementi treats only Br^{+1}, Br^{0}, and Br^{-1}. In Table II, we present total binding energies calculated for neutral iodine with the $5s^2 5p^5$ outer configuration. The changes in binding energy as valence p electrons are removed from the various halogens are shown in Figs. 6, 7, 8, 9, and 10. The changes as an f electron is removed from europium are shown in Fig. 11. Clementi's values are used for fluorine and chlorine. Bromine is a combination of the two, our results for $\Delta E_b^V(Br,i,2-1)$ having been multiplied by 0.973, the factor required

to make our values agree with Clementi's values for $\Delta E_b^V(Br,i,1\text{-}0)$. As abscissa we use the locations of the radial density maxima, to indicate the relative positions of various core levels with respect to the valence shell. Also, for qualitative reference we show the shift predicted classically if the valence electron were removed from a spherical shell at the radius of its density maximum.

There are several things to be noted in these free-ion calculations. The shift in binding energy increases with increasing degree of ionization. Also, all of the core levels are shifted by approximately the same amount (this is easily understood classically). The accuracy of this approximation is further emphasized for iodine by the values of Table V. For iodine all core levels shift by the same amount to within ±1.5%. Therefore, as long as we are concerned only with core levels, $E_b^V(I,i,Z\text{-}Z')$ need not be calculated for each i, but only using average values over the core. Such averages are presented for iodine in Fig. 10 using the iodide ion as a reference. The points form a smooth curve and graphical interpolation to non-integral Z is straightforward. The figures also show that the valence s binding energies are shifted less than the valence p energies for all the halogens. This further demonstrates the very uniform trends in shifts within this chemical group. The classical shifts are always 1-1/2 to 2 times larger than the neutral-atom quantum mechanical values, the direction of this difference arising from both the lack of attractive exchange in the classical model and the incorrectness of using the radial maximum location as an effective radius for the valence electron. The core level shifts also decrease with increasing atomic number within this chemical group. An examination of Clementi's tables shows that this trend holds true for all groups of

the periodic table with no partially filled d or f shells. Furthermore, there is up to a four-fold increase in the magnitude of free-ion shifts from left to right along a row in the periodic table, arising from the decrease in the average radius of the valence shell. Thus, for a given charge transfer in a free-ion the core shift will increase toward the upper right corner of the periodic table.

The 4f configurations of europium are known to be $4f^7$ in $EuAl_2$ [9] and $4f^6$ in Eu_2O_3,[10] with some indefinite amount of 6s or 6p character. We have calculated shifts accompanying removal of a 4f electron from both Eu^0 $4f^7 6s^2$ and Eu^{+2} $4f^7 6s^0$. Here again $\Delta E_b^V(Eu,i,\Delta Z=1)$ increases with increasing ionization, but the core levels are not all shifted the same amount. This is reasonable, as the 4f shell, unlike the halogen p shells is not an outer shell, and therefore there are filled "core" levels which have a good deal of density outside the 4f shell. This explanation is supported by the fact that the removal of the two outer 6s electrons shifts all the other binding energies by the same amount (12.17 eV) to within ±1%. The result indicates a potentiality in the electron spectroscopic technique of determining <u>which</u> outer electrons have gone into bonding from the relative changes of core electron binding energies. The classical approximation is reasonably good for the 6s shift: this would be expected since the 6s subshell is very far from the core shells, thereby minimizing quantum-mechanical corrections.

C. Madelung Energy Corrections

The calculation of $E_1 + E_2$ for ionic solids is very straightforward. We need the electrostatic potential energy of the ion in the lattice and the energy associated with electronic relaxation when a positive hole is formed. To a very good approximation the potential energy can be broken into three parts[29]: point-charge Coulombic interaction of the ions, repulsion and exchange interaction due to electron overlap, and attraction arising from Van der Waals' forces. The latter two terms act in opposite directions and we shall neglect them.

The third term remaining in the lattice potential energy is the point-charge Coulomb energy or Madelung energy,

$$E_M(Z) = e^2 \sum_k \frac{ZZ_k}{r_{Ak}} = e^2 Z \sum_k \frac{Z_k}{r_{Ak}} \quad . \tag{8}$$

Here r_{Ak} is the distance between the A ion of interest and some other ion k. The summation on k extends over all other ions in the lattice. Note that $E_M(Z)$ is proportional to Z. Thus the net Madelung contribution to $E_1 + E_2$ will be given by

$$-E_M(Z) + E_M(Z+1) = E_M(+1) \quad . \tag{9}$$

This is the Madelung potential of the positive hole formed by the photoelectric process. It is 5-10 eV in magnitude for the alkali halides. Neglecting electronic polarization effects (which we treat below), the binding energy in the solid becomes

$$E_b^V(A,i,X) = E_b^V(A,i,Z) + E_M(+1) \tag{10}$$

and the associated chemical shift between compounds X and Y is

$$\Delta E_b^V(A,i,X-Y) = \Delta E_b^V(A,i,Z-Z') + \Delta E_M(+1)_x - E_M(+1)_y \tag{11}$$

From Eq. (10) it is apparent that if $E_M(+1)$ is negative (as it will be at any site in the lattice which is normally positive) then the electron binding energy in the solid decreases relative to the free ion. The inverse occurs at sites which are normally negative.

If surface effects are neglected the sum in Eq. (8) is just one part of the multiple summation for the total Madelung energy of a unit cell[30]

$$E_M^u = \frac{e^2}{2} \sum_{i=1}^{\gamma}{}' \sum_k \frac{Z_i Z_k}{r_{ik}} \quad . \tag{12}$$

Here γ is the number of atoms in a unit cell and the prime excludes self-energy terms. We define the Madelung constant A_L in the usual way such that

$$E_M^u = -\frac{Ne^2 A_L}{L} \tag{13}$$

where L is some reference distance (often the smallest interatomic distance) and N is the number of molecules per unit cell. Comparison of Eqs. (12) and (13) shows that A_L is given by

$$A_L = -\frac{L}{2N} \sum_{i=1}^{\gamma}{}' \sum_j{}' \frac{Z_i Z_j}{r_{ij}} = \frac{-L}{2N} \sum_{i=1}^{\gamma}{}' Z_i \sum_j{}' \frac{Z_j}{r_{ij}}$$

$$A_L = -\frac{L}{2Ne^2} \sum_{i=1}^{\gamma}{}' E_M(Z_i) \quad . \tag{14}$$

From this form it is obvious that previously calculated Madelung constants cannot be used to predict individual $E_M(Z_i)$ values unless some relationship can be established between the various terms in the sum.[31] For the case of the sodium chloride and cesium chloride lattices for example, symmetry considerations require that $E_M(\text{cation})=E_M(\text{anion})$. For binary compounds it is also common to refer to the reduced Madelung constant[32]

$$\alpha_L = 2A_L/Z_a Z_c n \tag{15}$$

where Z_a is the anion charge, Z_c the cation charge and n is the number of atoms per molecule. Since $Nn = \gamma$, then

$$\alpha_L = -\frac{L}{Z_a Z_c \gamma e^2} \sum_{i=1}^{\gamma} E_M(Z_i) \tag{16}$$

applying this relation to the sodium chloride and cesium chloride lattices yields for the two types of lattice sites

$$\text{cation:} \quad E_M(+1) = -\frac{e^2\alpha_L}{L} \tag{17}$$

$$\text{anion:} \quad E_M(+1) = +\frac{e^2\alpha_L}{L} \tag{18}$$

These relations have been used together with a cycle quite similar to that in Fig. 5 to calculate valence electron band positions in the alkali halides.[21] However, in general the sum of Eq. (8) will have to be computed directly.

Because the unscattered photoelectrons are probably expelled from lattice sites located within several hundred Å of the surface, we cannot neglect

surface effects. Even if we assume that adsorbed or absorbed gas molecules are uncharged and contribute little to the Madelung energy of a site near the surface, the calculation of the energy would not be simple. It would require accurate knowledge of the mean free path for photoelectrons, and then an evaluation of the average value of the sum in Eq. (8) between the surface and a depth of one mean free path. Neither requirement can be met at this time, so we can make only a rough estimate of the surface correction. Neglecting entirely any adsorbed or absorbed material, sites at the surface will have approximately half the Madelung potential of sites very far from the surface. Therefore, our average must be between 0.5 and 1.0 times the bulk Madelung potential. It will be quite close to 1.0 if the mean free path, λ, is long compared to some radial distance r_{max} above which terms in the sum of Eq. (8) contribute negligibly to the Madelung potential. For simple ionic crystals, the work of Evjen[33] shows that r_{max} is roughly 5 times the lattice constant or the order of 20-50 Å. If mean free paths are several hundred Å, we can thus use Eq. (10) as is. However, to show that this correction is potentially important, we have also done calculations using 0.75 $E_M(+1)$, the value appropriate if $r_{max} \sim \lambda$. We might also note here that this surface correction is the closest analog to band bending near the surface permitted by our semi-classical model.

Of the five compounds of primary interest here (KI, KIO_3, KIO_4, $EuAl_2$, Eu_2O_3) the three iodine compounds readily lend themselves to calculation of the Madelung energy. KI has the NaCl structure and so Eqs. (17) and (18) can be applied directly. Also, it can be treated as a strictly ionic solid and used as a reference compound for chemical shifts of the other two. On the basis

of the Pauling electronegativity difference,[34] one would predict the charge on iodine to be about 0.5 in KI but Mössbauer, NMR, and dynamic quadrupole coupling measurements all indicate a value of 0.96-0.98.[8] Thus the point charges in the Madelung energy calculation can be taken as ±1 to a very good approximation. We might also note here that even if KI were not completely ionic the change induced in binding energies (and thus chemical shifts relative to KI) is less than a few tenths of an eV and negligible for our purposes. For example, if the KI lattice is treated as charges of magnitude 0.75 the net changes in iodine binding energies is only about 0.14 eV. This is due to the fact that lowering the negative charge on the iodine increases free-ion binding energies but also make it easier to form a positive hole at an iodine-site surrounded by several positive ions. The two effects thus tend to cancel, thereby explaining the small change in binding energy.

The KIO_3 lattice is more complicated, but tractable. The unit cell was for some time believed to be that of cubic perovskite ($CaTiO_3$) which contains one molecule, but recent studies indicate that it is a larger 8 molecule unit.[35] However, the larger unit cell does not permit simple calculation of $E_M(+1)$ and also represents only a slight distortion of ionic positions from the perovskite structure. Therefore, we select the perovskite structure for Madelung calculations. In this structure, each iodine is surrounded by 6 oxygens in a regular octahedron. A further complication is that we expect considerable covalent character of the I-O bonds. The Pauling electronegativity difference predicts only 0.25 fractional ionic character, for example. On the other hand, it is fairly certain that potassium exists as K^{+1} in the lattice. Therefore, we treat

the problem by calculating Madelung energies for a lattice of $K^{+1}\ I^{3Z-1}(O^{-Z})_3$ treating Z as a parameter. By taking advantage of the cubic symmetry of the perovskite lattice, the point-charge potentials at the K, I or O sites can be calculated in terms of the known Madelung constants of NaCl, CsCl, and Cu_2O and the charge Z.[36] The calculation of reference (36) was redone with our particular choice of ionic charges. The results at the potassium and iodine lattice sites are

$$K^{+1}:\quad E_M(+1) = \frac{e^2}{a}\{Z[A_a(NaCl) + 3A_a(CsCl) - A_a(Cu_2O)] - A_a(CsCl)\} \tag{19}$$

$$I^{3Z-1}:\quad E_M(+1) = \frac{e^2}{a}\{Z[A_a(CsCl) - A_a(Cu_2O)] + A_a(CsCl)\} \tag{20}$$

Here a is the length of the cubic cell edge. At Z = 0, the oxygens do not contribute to the Madelung potential and the energies reduce to those of the CsCl structure, as they must from the symmetry of the perovskite structure. With the known values a = 4.410 Å,[35] $A_a(NaCl) = 3.49512$,[32] $A_a(CsCl) = 2.03537$,[32] $A_a(Cu_2O) = 10.25949$,[32] $E_M(+1)$ was calculated as a function of Z. Since $E_b^V(I,i,Z)$ could be interpolated for all values of iodine charge, Eqs. (10) and (11) show that $E_b^V(I,i,KIO_3)$ and $\Delta E_b^V(I,i,KIO_3\text{-}KI)$ could also be calculated as functions of Z. For plotting we choose to use instead of Z the fractional ionic character f of the I-O bond. This is defined as f = Z/2 such that when f = 1 the iodine charge has the same value as its formal oxidation state (+5). We discuss below the factor of two difference between this definition and that of Pauling. The results of the calculations for the iodine core levels are shown in Fig. 12 for

both a full Madelung correction and a three-quarter Madelung correction. The points on each curve are the locations at which the iodine has zero charge. The finite curvature of both plots is due to the curvature in Fig. 10, since the Madelung corrections are strictly linear in f. The minimum in the fully corrected curve arises since the Madelung correction of Eq. (20) steadily lowers the binding energy as f increases, whereas the concomitant increase of the charge on the iodine atom tends to raise the binding energy but at a different rate. The importance of the amount of Madelung correction used is also emphasized here, since the two different curves are 3 eV apart by f = 0.25. This is certainly not negligible with respect to chemical shifts.

For the case of KIO_4, the actual crystal structure is also too complicated to permit easy calculation of $E_M(+1)$. The unit cell is that of scheelite ($CaWO_4$) and contains four molecules.[37] Each iodine is surrounded tetrahedrally by four oxygens and the I-O bonds will again be considerably covalent. Potassium can again be assumed to exist as K^{+1}, and the lattice can therefore be treated in first approximation as being composed of K^{+1} and $(IO_4)^{-1}$ point charges. We can then consider the interaction of each iodine with its four nearest neighbor oxygen, and assign charges of 4Z - 1 to iodine and -Z to the oxygens. This two-step calculation should give a reasonably good estimate of the actual Madelung potential seen by an iodine atom. The first portion of the Madelung energy was obtained from the reduced Madelung constant of scheelite. This constant has been calculated by treating the WO_4^{-2} ions as point charges.[38] The symmetry of this point charge lattice requires that $E_M(\text{anion}) = E_M(\text{cation})$ so that Eqs. (17) and (18) are valid. The reduced Madelung constant is $\alpha_r = 1.61550$ where r = 4.07 Å,

the shortest anion-cation distance for the $K^+(IO_4)^-$ point charge lattice. The nearest neighbor correction could be made quite easily since the I-O distance is known to be 1.80 Å.[37] The chemical shift $\Delta E_b^V(I,i,KIO_4\text{-}KI)$ was thus calculated as a function of f and the results appear in Fig. 12. The correction has much less effect for KIO_4. This is reasonable since the Madelung energy was calculated treating only the iodine nearest neighbors in detail.

Having treated the iodine core levels in KI, KIO_3, and KIO_4, we turn briefly to the potassium levels. Since potassium was assumed to exist as K^{+1} in all three, any shifts will be due to Madelung and possibly polarization corrections. Madelung corrections were calculated for KF, KCl, KBr, KI, KIO_3, and KIO_4. The potassium halides were treated as K^{+1} X^{-1} lattices. For KIO_3 a rough estimate of Z was obtained by directly comparing the experimental and fully corrected theoretical shifts in Fig. 12. This Z value (1.32) was then used in Eq. (19). For KIO_4, Z was estimated in the same way. Then a calculation similar to that for iodine was made. The Madelung energy was assumed to be the $K^+(IO_4)^-$ point charge contribution corrected exactly for the eight nearest neighbor IO_4^- groups. The chemical shifts relative to KI are presented in Table VI. On the basis of this approximate calculation there are clearly non-negligible shifts of the potassium levels. The shifts of potassium levels are further verified for the potassium halides where our lattice model is much better and the shift quite large for KF. We mention this to demonstrate that the use of some common constituent in a group of compounds as a reference level is inherently inaccurate from a theoretical point of view. Our experimental results also bear out this sensitivity of the potassium levels to chemical environment. The fact

that the sodium $1s_{1/2}$ level has been measured in NaCl, $NaClO_2$, $NaClO_3$, and $NaClO_4$ and found to be the same within experimental error (±0.4 eV)[7] would seem to indicate the shifts are fortuitously small for these compounds. A general neglect of them is not valid, however.

D. Charged-Shell Approximation

From Figs. 6, 7, 8, 9, and 11, it is apparent that a strictly classical model can be used to give a rough estimate of the core electron binding energy shift accompanying a change in the charge state of a free atom or ion. We can also use a partially classical model to estimate the shifts that accompany charge transfer within an atomic complex. This model provides some insight into the origins of the observed shifts and emphasizes their sensitivity to covalency.

Consider an atom A in some solid compound or some molecular complex. It will be surrounded by a set of nearest neighbors which are primarily responsible for the way in which the valence electrons of A are distorted in the bonding process. It is thus a fair approximation to consider only the nearest neighbor effects in calculating core shifts in A. (From the point of view of our Madelung calculation, this amounts to truncating the Madelung sum at one term.) To do this, we can use a spherical shell to approximate the charge in bonding orbitals with its nearest neighbors. For simplicity, we might consider the case where A has only B atoms as nearest neighbors. Then the complex of interest is $(AB_n)^m$ where n is the no. of nearest neighbors and m represents the net charge of the complex. The charge m can thus have any positive or negative value (including

0 for a neutral molecule). If all B atoms are at roughly the same distance from A we can denote the nearest neighbor separation by r_{AB}. The charge transfer due to chemical bonding can be approximated by a non-integral transfer of charge $-e\alpha$ (α can be positive or negative) from the unperturbed free-ion valence shell of A to a spherical shell of radius r centered at the atom A. The charge em we take somewhat arbitrarily to be on the valence shell of A. This parallels our treatment of KIO_3 where the ionic charges in IO_3^- were taken to be I^{3Z-1} and O^{-Z}. The model thus obtained is shown in Fig. 13 for octahedral $(AB_6)^m$. The radius r should be less than or equal to r_{AB}. The case $r = r_{AB}$ would correspond to a very highly ionic bond, since charge would be transferred essentially to the location of the unperturbed free-ion valence shell of B. A core electron binding energy for A is thus given by

$$E_b^V(A,i,AB_n{}^m) = E_b^V(A,i,m+\alpha) - \frac{e^2\alpha}{r} \quad . \tag{21}$$

The second term is a repulsive or attractive potential due to the charge shell at r. It always acts in the opposite direction to the change in free-ion bonding energy $\Delta E_b^V(A,i,\alpha-0)$. Such potentials are undoubtedly the main reason that measured chemical shifts are always much less than expected from free-ion calculations. That is, in free-ion calculations the electronic charge is removed to infinity, when actually it is only moved by distances of the order of r_{AB}.

Madelung potential calculations could not be easily made for the two europium compounds investigated, largely because of the complexity of their

crystal structures. $EuAl_2$ has the $MgCu_2$ structure with 8 molecules per unit cell[39] and Eu_2O_3 has the cubic bixbyite (Fe_2O_3) structure with 16 molecules per cell unit.[40] An additional difficulty is that both compounds have an indefinite amount of metallic or covalent character and neither would serve as a clean cut reference compound analogous to KI. We can however make a rough calculation using the charged shell approximation in place of the Madelung correction. That is, we first assume that the electronic shell n = 6 changes negligibly in density distribution in going from $EuAl_2$ to Eu_2O_3. Then the chemical shift will be due to transfer of one 4f electron into some sort of chemical bond, and will be given by approximately by

$$\Delta E_b^V(Eu,i,Eu_2O_3\text{-}EuAl_2) \cong \Delta E_b^V(Eu,i,3\text{-}2) + \Delta E_M(+1) \quad . \tag{22}$$

We can approximate $\Delta E_M(+1)$ by considering only nearest neighbor interaction as discussed previously. Then a simple extension of the charged shell approximation gives $\Delta E_M(+1) \sim -\frac{e^2}{r}$ if r is the average radial distance of the bonding 4f electron in Eu_2O_3. Using this approximation on the $3d_{5/2}$ level showed that a 9.6 eV chemical shift corresponds to $r \simeq 1.3$ Å. We discuss this in relation to our experimental values in Sec. VI.

An alternative approach for discussing the europium data would be to assume that in metallic $EuAl_2$ the Madelung correction is much reduced so that Eu^{+2} free ion binding energies are approximately correct. Then the chemical shift between $EuAl_2$ and Eu_2O_3 is due to the free ion shift $\Delta E_b^V(Eu,i,3\text{-}2)$ and the Madelung energy of Eu_2O_3. Since the former is approximately 20 eV a Madelung

energy of approximately 10 eV is required to give the net shift of 10 eV we have observed. As this is the approximate magnitude of Madelung energies for most crystals, this explanation also is consistent with our data, although rather qualitative.

E. Relaxation Corrections

The maximum value of the relaxation energy can be calculated by assuming that electronic polarization about the positive hole has proceeded to equilibrium. In order for this full correction to apply, equilibrium must be reached in a time short compared to both the electron escape time and the hole lifetime. To calculate this correction we note that the net relaxation energy will be the energy associated with the polarization by the positive hole of the electron clouds on every other ion in the lattice. Relaxation within the ion of interest was considered above in the discussion of Koopmans' Theorem. We may approximate the final state as a spherical shell of unit charge in a continuous dielectric medium.[21] The radius R_A of the spherical shell will be quite close to the ionic radius of A^Z. Since we are neglecting nuclear relaxation, it is the dielectric constant K at optical frequencies (10^{15} cps) much larger than lattice vibration frequencies (10^{13} cps) that is appropriate. The polarization energy is

$$E_p = -\frac{1}{2}\frac{e^2}{R_A}\left(1 - \frac{1}{K}\right) \qquad (23)$$

with negative sign so as to lower $E_b^V(A,i,X)$ relative to $E_b^V(A,i,Z)$. A more rigorous method of calculating E is also given in Ref. 21. Now E_p can be added to Eqs. (10) and (11) to give binding energies and chemical shifts that are maximally corrected for polarization

$$E_b^V(A,i,X) = E_b^V(A,i,Z) + E_M(+1) + E_p \tag{24}$$

$$\Delta E_b^V(A,i,X-Y) = \Delta E_b^V(A,i,Z-Z') + E_M(+1)_x - E_M(+1)_y + E_{px} - E_{py} \tag{25}$$

To get an idea of the magnitude of polarization corrections, calculations of E_p were made on all the alkali iodides, KIO_3 and KIO_4. For R_A a value of 0.9 times the iodine-nearest neighbor distance was used. This value is suggested by the more rigorous method of calculating E_p mentioned above. The values used in the calculation and the results are presented in Table VII. The corrections due to polarization for these compounds are relatively small, being less than 1.0 eV except for KIO_4. Since it is probable that only some fraction of these values is applicable, we will neglect polarization for these compounds. In general, however, the magnitude of such corrections should be checked whenever possible, as they could easily be comparable to a small chemical shift.

We should also note at this point that if one is interested in a chemical shift between two atoms of the same type which occupy chemically different sites in the same molecule or solid, the corrections due to shifting reference level and electronic polarization can be neglected to a very good approximation.

Surface effects are also much easier to treat in this case, if they need to be considered at all. Such cases represent the most clear-cut applications of the technique.

VI. DISCUSSION

A. Halogens

In Fig. 7, we compare experimental values for $\Delta E_b^f(Cl,i,NaClO_4\text{-}NaCl)$ from the work of Fahlman, Carlsson, and Siegbahn[7] with theoretical free-ion values at various ionic charges. For the two levels considered ($1s_{1/2}$ and $2s_{1/2}$) the shifts are very nearly the same (9.6 eV and 9.5 eV, respectively) in agreement with the trend predicted by the free-ion calculations. Since the corrections embodied in $\Delta(E_1+E_2)$ and $\Delta(\phi_c)$ are the same for all levels, it is to be expected that relative shifts of different levels could be determined from free-ion calculations. If the actual ionic charge is roughly linear in v, this explains why Eq. (7) can be used with reasonable success to predict shifts. For chlorine, the proportionality constant in Eq. (7) was calculated as about 0.12, a little larger than that obtained by Lindgren[24] for sulfur.

In Fig. 9, our experimental values for $\Delta E_b^f(I,i,KIO_4\text{-}KI)$ are compared to free-ion values. To within experimental error, all the core level shifts are the same, again in agreement with free-ion predictions. For iodine, the proportionality constant in Eq. (7) is about 0.07.

In Table II, we have compared our calculated free-ion binding energies for I^0 with those measured in KI. While it is obvious from Eqs. (10)

or (24) that this comparison is not rigorous, the net correction to the I^o values is only about 1 eV, which is close enough for present purposes. Since no spin-orbit coupling was included in the calculation, we have appropriately averaged $\ell+1/2$ and $\ell-1/2$ experimental values for approximate comparison.[41] The agreement is good, especially in view of our use of a minimal basis set. The large discrepancies for the 2s, 2p, and 3s levels can probably be explained almost entirely by relativistic effects, since the relativistic corrections computed by Herman and Skillman[42] in this region of atomic number are approximately 360 eV, 150 eV, and 80 eV respectively, and in the proper direction.

In Fig. 12 the experimental shifts for KIO_3 and KIO_4 are compared to the values we have calculated as a function of f. The values of f and iodine charge, which correspond to the observed shifts are summarized in Table VIII. The results are compared to those obtained via Mössbauer measurements on the same compounds.[8] The agreement is satisfactory in the sense that Madelung corrections in the plausible range can bring our derived values of f and z into good agreement with the Mössbauer results. The sensitivity of both f and z to the magnitude of this correction indicates, however, that in partially ionic solids like KIO_3 and KIO_4 more sophisticated data treatment will be necessary before these parameters can be derived with high accuracy. One possibility would be to consider the shifts of more than one atom common to several compounds, as for example, K and I in KI, KIO_3, and KIO_4. The f value would thus be selected so as to best fit two experimental shift values for each compound. Such a calculation was made for these compounds, but the f values obtained were negligibly different from those of the one atom fit. This is due

to the much greater sensitivity of iodine binding energies to changes in f as compared to potassium. For sets of compounds where two constituents both show comparable sensitivity however, such calculations should permit more accurate f or charge estimates.

It should also be noted that our calculations have all been based on removal of only p electrons from the valence shells of a halogen atom. For any type of hybridized bonding, this of course is not true. We have made free-ion calculations which show approximately a 10% difference in the core electron binding energy shifts of iodine between 5s removal and 5p removal, so hybridization among these levels could introduce a small error in our results. Our approximation of only p removal is quite good for KIO_3 but for KIO_4 the tetrahedral bonding is believed to be sp^3 so 1/4 of the charge is removed from the 5s shell.[8] This fraction would introduce only about a 0.2 eV error in our chemical shift calculations and so is not significant for the present. Such differences should be kept in mind however, and suggest the possibility of determining which valence electrons have gone into a bond by the magnitude of a chemical shift. For example, in europium a free-ion shift for 6s removal is approximately 6 eV and this is 14 eV smaller than that for 4f removal. This would give rise to very large differences in a calculated chemical shift depending on which type of bonding was assumed. For example, the shift of 9.6 eV between $EuAl_2$ and Eu_2O_3 could not be explained at all by a transfer of one 6s electron into bonding positions and further validates the $4f^7$ and $4f^6$ configuration assignments of these compounds.

The iodine shift results for the potassium salt of p-iodobenzoic acid are presented primarily to indicate that iodine shifts can be measured in organic

compounds with a high degree of covalent bonding. This has also been previously demonstrated for organic compounds containing sulfur.[4] With further refinements such measurements might establish the chemical state of some constituent in an organic molecule. For example, our measurements show that the oxidation state of iodine is in the range -1 to +1 in this compound. Further applications of this type are discussed in Sec. VIC.

The experimental potassium shifts are in reasonable agreement with the theoretical predictions of Table VI. The direction and approximate magnitude is correct for KIO_3 where our Madelung treatment is relatively accurate. The direction is wrong for KIO_4, but this is not surprising since the shift is small and our theoretical treatment is very approximate for this case. This lack of agreement for KIO_4 demonstrates the importance of an accurate Madelung calculation.

B. Europium

In Fig. 11, we compare experimental shifts of the $3d_{3/2}$, $3d_{5/2}$, and $4p_{3/2}$ levels to the free-ion values. Due to difficulties in resolving the

photoelectron peaks from other levels, we do not have sufficient data to determine whether or not the relative shifts of different levels are as predicted by the free-ion values. If they are, the proportionality constant in Eq. (7) is about 0.46, a much larger value than found for sulfur, chlorine, or iodine. This is to be expected as one 4f electron is transferred in going from +2 to +3 europium, whereas the corresponding transfer for a unit change in the oxidation state of the other atoms is probably much smaller. For iodine, for example, Table VIII indicates less than 0.5 electrons become involved in bonding per unit change in oxidation number.

The radius obtained in our approximate charged-shell treatment of these europium compounds is consistent with a simple picture of chemical bonding. In order to obtain the proper chemical shift one 4f electron had to be transferred into a spherical shell at approximately a 1.3 Å radius. Since this spherical shell must somehow approximate the bonding orbitals in Eu_2O_3, we would expect it to be somewhere in between a central europium atom and the atoms around it. As the Eu-O distance in Eu_2O_3 is 2.3 Å, this is indeed the case. While this charged-shell model is a gross simplification of the actual situation, it nevertheless gives semi-quantitative answers and some insight into the physics of a chemical shift of core electron binding energies.

C. Further Applications of the Photo-electron Spectroscopic Technique

The curves of Fig. 12 for KIO_3 and KIO_4 indicate a high sensitivity of the core-electron chemical shift to the fractional ionic character of the I-O bonds in these compounds. This sensitivity suggests that ΔE_b^V might serve as a useful operational definition of ionic character. To evaluate this possibility it is helpful to review the types of measurements on which the concept of ionic character is based, comparing the quantities which are measured in each case.

Basic to any discussion of chemical bonding is the question of electronic charge transfer among the various atoms. Such transfer must of course be qualified by noting that electrons in solids do not "belong" to any particular atom and that charge transfer due to bonding is simply an alteration of electronic probability distributions. Thus some approximation is necessary even in the discussion of highly ionic solids where the partitioning of the probability distribution of electrons among various atoms is certainly not obvious, nor even unique. Therefore, one should not be at all dogmatic about conclusions involving small changes (~0.01) in the fractional ionic character f, but on the other hand large changes (~0.1) in the value of f can give very concrete information about the bonding in different compounds. Several models have been used to deduce f from experimental data.

Two well-known methods for assessing ionic character are based on electric dipole moments[34] and quadrupole coupling constants.[43] The first method is sensitive to all electrons, but is subject to uncertainties in polarization corrections if one uses it to extract ionic character. It also is limited in application, since many symmetrical complexes do not have non-zero electric dipole

moments. The quadrupole method is free of this latter objection (for example, Cl in liquid $SnCl_4$), but is totally insensitive to the distribution of s electrons. Also, the atom to be investigated must possess an isotope with nuclear spin ≥ 1. Though not very generally applicable, both of these methods give useful semiquantitative information. The discrepancy of about 30% between the two electronegativity-ionic character relations that the two methods give for diatomic halides[44] is about the agreement one might expect.

More recently, isomer shifts derived from Mössbauer spectra have provided a technique for the measurement of ionic character in inorganic compounds.[45] The isomer shift δE is directly proportional to the difference of the electron densities at the same nucleus in two different compounds, that is, $\delta E \propto \Delta\psi^2(0)$. Because of shielding and relativistic effects however, $\Delta\psi^2(0)$ depends not only on the number of s electrons in the valence shell but also on the population of all other electrons in the valence shell. To a first approximation the isomer shift for an atom with s and p electrons in the valence shell can thus be written as

$$\delta E = A(\Delta n_s) + B(\Delta n_p) \tag{26}$$

where $\Delta n_s(\Delta n_p)$ is the difference in number of s(p) electrons in the valence shells of the two compounds. For a given isotope A and B may be determined empirically by measurements on certain calibration compounds. With enough additional information (usually involving a bonding model) it is then possible to determine n_s and n_p for a given compound from measured δE values. This method is most sensitive to s electron transfer. It is also not widely applicable, since an isotope must

be found which possesses a Mössbauer transition. However, for cases in which Mössbauer results can be compared to those of the two previously mentioned techniques, the agreement is satisfactory.

The photoelectron spectroscopic technique used in this investigation yields the binding energies of core electrons and therefore is directly relatable to the Coulomb and exchange interactions within the parent atom in the lattice. In our theoretical treatment, we chose to divide this potential into two parts: the detailed quantum mechanical interaction of all particles in the parent atom and the classical interaction of all other atoms in the lattice. The electronic density on all other atoms was split up according to a self-consistent scheme. The charges Z_i at the various sites will generally not be integral, but electronegativity considerations combined with the condition of electroneutrality should often permit the establishment of relationships between the various Z_i (as, for example in our treatment of KIO_3). In addition, if chemical shifts were measured for more than one atomic species common to a set of compounds as we have discussed earlier the unique determination of ionic charges might be possible. That is, the comparison of experimental shifts for these atomic species with theoretical curves such as Fig. 12 for each species (derived either from the cycle of Fig. 5 or more accurate MO or solid-state calculations) might permit a unique assignment of charges. This would eliminate the necessity of assuming potassium to be K^{+1} for example and extend the applicability of the technique to compounds with little ionic character.

While it is not our intention to make a detailed comparison of this method with the three mentioned above, it should be clear that ΔE_b^V (or to a first approximation ΔE_b^f) measurements are more generally applicable and at the same time less

model-dependent than the others. One may obtain from ΔE_b studies a direct evaluation of the charge on each atom with a minimum of assumptions concerning the bonding orbitals. These charges may subsequently be interpreted in terms of fractional ionic character or any bonding model.

The application of the photoelectron spectroscopic technique to structural problems of molecular biology or biochemistry is potentially of great utility. In these problems one is often interested in large molecules with considerable covalent bonding, but also relatively few active sites of different chemical character. For such cases intramolecular interactions would be of prime importance, and perhaps only those due to the nearest neighbors of a given active would need to be considered. The Madelung formalism would not be appropriate for such problems, and a molecular-orbital approach would be the most accurate technique. To a first approximation, our charged-shell approximation might also give useful results. In addition, it seems fairly certain that the mean free path for discrete energy losses would be very long, so that surface effects would be minimized. For example, the mean free path in polystyrene is approximately 10,000 Å for the only discrete loss which would interfere with photoelectron spectra considerably.[23] These facts could much simplify theoretical calculations for certain cases and permit assignment of charges to different atoms. We discuss below several examples where photoelectron spectroscopy seems particularly suited.

Metal ions are ubiquitous constituents of biological systems serving a variety of functions. Alkaline earth ions including magnesium and calcium activate some enzymes and magnesium is an essential constituent of chlorophyll.

The transition metal ions, zinc, copper, vanadium, iron, manganese, and molybdenum participate in a number of biochemical processes including enzymic reactions, electron transport reactions, and oxygen transport reactions. In many instances these ions either exhibit no spectroscopic evidence for their presence or lose such spectroscopic features in one of their usual oxidation states. The photoelectron spectroscopic method would provide direct positive evidence for the presence of ions in their various oxidation states and offers an additional method for the study of the coordination chemistry of metal ions.

The structural integrity of many proteins is dependent on their sulfur content, especially the disulfide linkages. Non-degradative methods for the analysis of sulfur are not readily available; there are no optical transitions specifically attributable to sulfur and the only sulfur isotopes amenable to study by nuclear magnetic resonance occurs in low natural abundance with a small nuclear gyromagnetic ratio and a spin and quadrupole moment such as to largely preclude high resolution nmr spectra. The photoelectron spectroscopic method has already demonstrated its usefulness in the study of sulfur chemistry[4] and, in particular, is capable of distinguishing sulfur in a disulfide linkage.[46] It should thus be possible to determine the number of disulfide bonds in an intact protein, the ratio of disulfide to sulfide, and to verify if the same number of such bonds were present after reconstitution experiments.

Many investigators are currently focusing attention on a class of non heme iron proteins, called Ferredoxins,[47] which act as electron transport proteins in both photosynthesis and bacterial metabolism. The common characteristic of these proteins is their content of from two to seven iron atoms together

with a number of sulfur atoms. The electron spectra of these proteins will provide additional evidence for the presence or absence of chemical equivalence of the iron atoms both before and after reduction. There is slight evidence from Mössbauer spectroscopy for non-equivalence of the iron atoms. The study of the sulfur spectra of these proteins should prove especially rewarding as there is virtually no direct information on the nature of the sulfur-iron interaction.

VIII. CONCLUSIONS

We have studied the problems associated with the extraction of information about chemical bonding from core electron binding energy shifts measured by the photoelectron spectroscopic technique. Our major conclusions are summarized below:

1. Binding energy shifts may not be compared directly to theoretical calculations on free-ions to extract useful information about bonding. This is explicitly demonstrated in the energy cycle we have used for the approximate calculation of binding energies in crystalline solids. The major correction to be considered for this case is the Madelung energy. Other corrections of potential importance are those due to surface effects, the reference level for binding energies, and electronic relaxation, but these are minimized for shifts measured within one molecule or solid.

2. For ionic solids the Madelung energy can be several electron volts and must always be considered. The magnitude of this correction is somewhat uncertain due to the proximity of the photoelectron-producing sites to the surface.

3. The reference level for binding energies is somewhat in doubt for dielectrics. Local charging-up of the sample, for example, can shift this reference level. In addition, the experimental reference level (the Fermi level) is not easily obtained theoretically. The use of some electronic level in a simple ion common to all compounds such as K^{+1} or Na^{+1} as a reference level is not valid and can lead to errors up to several eV. This is an obvious consequence of the Madelung energy variation and is also verified experimentally.

4. A reliable correction for electronic relaxation is elusive, but approximate calculations yield upper limits of approximately 1 eV for the iodine compounds of interest here.

5. The charged shell model for simple atomic complexes can be used to give semi-quantitative estimates of chemical shifts. It also illustrates the relation between shift magnitude and bond polarity in such complexes.

6. Free-ion Hartree-Fock calculations indicate several trends of importance for shift measurements in solids. The electron binding energy shifts accompanying the removal of an outer valence electron vary little throughout the core; this is true to much less degree for the removal of an inner valence f electron. These shifts show a decrease in magnitude with increasing atomic number for a given chemical group (for example, from 20 eV in fluorine to 10 eV in iodine). Variation across the periodic table is also found, there being an increase from left to right. The shifts are relatively insensitive to the orbital quantum number of the electron removed, but quite sensitive to its principal quantum number, as illustrated by the 4f and 6s electrons of europium. Relativistic and Koopmans' Theorem corrections should be relatively unimportant for chemical shift determinations.

7. The experimentally measured shift for iodine is approximately 0.8 eV per unit change in formal oxidation number, the corresponding shift for europium between +2 and +3 states is 9.6 eV. The 12-fold difference can be qualitatively explained in terms of our theoretical models. Within experimental accuracy, all the core levels of iodine are shifted by the same amount and this also is consistent with theory.

8. The prediction of atomic charge as we have done for KI, KIO_3, and KIO_4 needs some refinement before it can give detailed information about bonding. In particular, by measuring all core atomic levels in each of several compounds a much more accurate charge assignment could be made. The agreement between our charge values and those derived from Mössbauer work is encouraging.

9. Careful study will be necessary before significance can be attached to shifts of 1 eV or less measured between two different compounds. However, shifts of similar magnitude within the same molecule or solid have been reliably detected and are far easier to relate to bonding phenomena alone. Biology and biochemistry present some interesting problems of this latter variety.

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Footnotes and References

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Table I. Experimental binding energy shifts relative to KI for various iodine core levels in the potassium salt of p-iodobenzoic acid (KIBA), potassium iodate, and potassium periodate. The number of individual binding energy measurements for each level in a compound is also given.

Level (i)(Radiation)	Compound(X)	Number of Measurements	$\Delta E_b^f(I,i,X\text{-}KI)$ (eV)
$2s_{1/2}(CuK\alpha_1)$	KI	4	0
	KIBA	1	-0.3
	KIO_3	4	5.5
	KIO_4	3	5.8
$2p_{1/2}(CuK\alpha_1)$	KI	2	0
	KIO_3	2	5.7
	KIO_4	2	5.5
$2p_{3/2}(CuK\alpha_1)$	KI	4	0
	KIBA	2	0.8
	KIO_3	5	5.5
	KIO_4	4	6.4
$3d_{3/2}(CrK\alpha_2)$	KI	2	0
	KIBA	2	-0.9
	KIO_3	1	2.4
	KIO_4	2	6.1
$3d_{5/2}(CrK\alpha_1)$	KI	2	0
	KIBA	3	0.2
	KIO_3	3	4.6
	KIO_4	4	6.1

Table I. Continued

Level (i)(Radiation)	Compound(X)	Number of Measurements	$\Delta E_b^f(I,i,X\text{-}KI)$ (eV)
$4s_{1/2}(CrK\alpha_1)$	KI	2	0
	KIBA	1	-0.1
	KIO_3	2	5.3
	KIO_4	4	6.5
$4p_{3/2}(CrK\alpha_1)$	KI	1	0
	KIO_3	1	5.1
	KIO_4	3	5.7
$4d_{3/2-5/2}(CrK\alpha_1)$	KI	2	0
	KIBA	1	-0.9
	KIO_3	2	5.1
	KIO_4	3	5.9

Table II. Experimental iodine binding energies in potassium iodide (Fermi reference level) and theoretical binding energies for the free iodine atom (vacuum reference level). All experimental values are from this work except those with an asterisk; these come from ref. 1.

Level (i)	Experimental Binding Energies $E_b^f(I,i,KI)$ (eV)		Theoretical Binding Energies $E_b^v(I,i,0)$ (eV)
$2s_{1/2}$	5191.6		4861.1
$2p_{1/2}$	4856.2	4659.4	4607.5
$2p_{3/2}$	4561.0		
$3s_{1/2}$	1072*		998.8
$3p_{1/2}$	937.0	899.5	890.7
$3p_{3/2}$	880.7		
$3d_{5/2}$	635.5	626.2	640.5
$3d_{5/2}$	623.5		
$4s_{1/2}$	190.5		184.4
$4p_{1/2-3/2}$	123*		142.4
$4d_{3/2-5/2}$	54.4		56.9
$5s_{1/2}$	16*		18.8
$5p_{1/2-3/2}$	4*		8.6

Table III. Experimental binding energy shifts relative to $EuAl_2$ for various europium core levels in Eu_2O_3. The number of individual binding energy measurements for each level in a compound is also given.

Level (i) (Radiation)	Compound	Number of Measurements	$\Delta E_b^f(Eu,i,Eu_2O_3-EuAl_2)$ (eV)
$3d_{3/2}(CrK\alpha_1)$	$EuAl_2$	1	0
	Eu_2O_3	1	10.2
$3d_{5/2}(CrK\alpha_1)$	$EuAl_2$	4	0
	Eu_2O_3	4	9.6
$4p_{3/2}(CrK\alpha_1)$	$EuAl_2$	1	0
	Eu_2O_3	1	9.2

Table IV. Calculated binding energies for the fluoride and iodide ions, showing both the Koopmans' theorem energy eigenvalues and more correct results obtained by taking differences of total energies. The ratio of Koopman's theorem binding energies to correct binding energies is also given.

Level (i)	E_b^v(Koop) (eV)	E_b^v(Diff) (eV)	$\frac{E_b^v(\text{Koop})}{E_b^v(\text{Diff})}$
$F^{-1}2s^2 2p^6$:			
1s	699.1	675.2	1.035
2s	22.7	19.9	1.141
$I^{-1}5s^2 5p^6$:			
2s	4852.3	4816.5	1.008
2p	4598.7	4560.1	1.008
3s	990.0	974.1	1.016
3p	881.9	865.4	1.019
3d	631.7	613.7	1.029
4s	175.5	169.3	1.037
4p	133.6	127.6	1.047
4d	48.1	42.3	1.135
5s	10.7	9.9	1.082

Table V. Calculated binding energy shifts between various free ion states of iodine.

$I^{-1}5s^25p^6$	$I^0 5s^2 5p^5$	$I^{+1}5s^25p^4$	$I^{+2}5s^25p^3$	$I^{+3}5s^25p^2$	$I^{+4}5s^25p^1$
Level (i)	$\Delta E_b^v(I,i,0-[-1])$ (eV)	$\Delta E_b^v(I,i,1-0)$ (eV)	$\Delta E_b^v(I,i,2-1)$ (eV)	$\Delta E_b^v(I,i,3-2)$ (eV)	$\Delta E_b^v(I,i,4-3)$ (eV)
2s	8.80	9.90	10.93	12.23	13.14
2p	8.79	9.87	10.93	12.19	13.16
3s	8.83	9.89	10.91	12.15	13.04
3p	8.79	9.87	10.87	12.12	13.01
3d	8.78	9.87	10.89	12.15	13.06
4s	8.85	9.87	10.82	11.97	12.78
4p	8.84	9.86	10.79	11.92	12.73
4d	8.84	9.85	10.78	11.92	12.72
5s	8.10	8.65	9.22	9.77	10.21
5p	8.39	9.37	10.73	9.44	9.90

Table VI. Calculated and experimental binding energy shifts of potassium core levels for the potassium halides, KIO_3, and KIO_4. KI is used as the reference compound.

Compounds (X)	$\Delta E_b^V(K,i,X-KI)$ (calc.)	$\Delta E_b^f(K,i,X-KI)$ (expt.)
KF	-2.331	---
KCl	-0.885	---
KBr	-0.520	---
KI	0	0
KIO_3	-2.353	-1.3±0.2
KIO_4	0.497	-1.3±0.2

Table VII. Polarization corrections to iodine binding energy shifts for the alkali iodides, KIO_3, and KIO_4. KI is used as the reference compound.

Compound (X)	$E_{px}-E_{p-KI}$
LiI	-0.523
NaI	-0.202
KI	0
RbI	0.067
CsI	0.065
KIO_3	-0.836
KIO_4	-1.368

Table VIII. Comparison of present results for fractional ionic character and iodine charge in KIO_3 and KIO_4 to those obtained from Mössbauer measurements in Ref. 8 . Our results for both both the full and three-quarter Madelung correction are given.

Compound	f	Iodine Charge
Full Madelung:		
KIO_3	0.67	2.99
KIO_4	0.48	2.86
3/4 Madelung:		
KIO_3	0.35	1.10
KIO_4	0.28	1.24
Mössbauer:		
KIO_3	0.31	0.83
KIO_4	0.31	1.44

Figure Captions

Fig. 1. Schematic illustration of the experimental setup.

Fig. 2. Energy diagram for the photoelectric process in a semiconducting or insulating source (solid compound X). The photoemission is from some arbitrary core level i of an atom A in solid X.

Fig. 3. Photoelectron peaks from the $I_{2p_{3/2}}$ level in KI and KIO_4. $CuK\alpha_1$ radiation was used for excitation.

Fig. 4. Photoelectron peaks from the $Eu3d_{5/2}$ levels in $EuAl_2$, Eu-metal and Eu_2O_3. An Eu-metal sample was first examined with minimal oxidation and then again after prolonged exposure to air. The exciting x-ray lines were $CuK\alpha_1$ and $CuK\alpha_2$. The probable sources of the three peaks are noted in the lower portion of the figure.

Fig. 5. Energy cycle for calculating the binding energy of core electron i of atom A in the solid lattice of compound X. Z is the charge on A in the lattice. E_1 is the energy required to remove A from the lattice leaving a lattice vacancy. E_2 is the energy required to insert A^{z+1} back into that vacancy. $E_b^V(A,i,Z)$ is a free-ion binding energy.

Fig. 6. Calculated binding energy shifts due to removing a ~2p electron from various free-ion configurations of fluorine. The 2s subshell is full in all configurations, so $2=2p^3$, $1=2p^4$, $0=2p^5$, and $-1=2p^6$. The shift values are from calculations by Clementi in Ref. 25. As abscissa we use the location of the radial density maximum for each level. Also, the classical

shift due to removing an electron from a spherical shell at the location of the 2p maximum is given.

Fig. 7. Calculated binding energy shifts due to removing a 3p electron from various free-ion configurations of chlorine. The 3s subshell is full in all configurations, so $2=3p^3$, $1=3p^4$, $0=3p^5$ and $-1=3p^6$. The shift values are from calculations by Clementi in Ref. 25. The abscissa and classical shift are analogous to those in Fig. 6. Also shown are experimental shifts between NaCl and $NaClO_4$ from Ref. 7.

Fig. 8. Calculated binding energy shifts due to removing a 4p electron from various free-ion configurations of bromine. The 4s subshell is full in all configurations, so $2=4p^3$, $1=4p^4$, $0=4p^5$ and $-1=4p^6$. The shift values are a combination of our values and those of Ref.25 as noted in the text. The abscissa and classical shift are analogous to those in Fig. 6.

Fig. 9. Calculated binding energy shifts due to removing a 5p electron from various free-ion configurations of iodine. The 5s subshell is full in all configurations so $4=5p^1$, $3=5p^2$, $2=5p^3$, $1=5p^4$, $0=5p^5$ and $-1=5p^6$. The shift values are based on our calculations. The abscissa and classical shift are analogous to those in Fig. 6. Also shown are our experimental shifts between KI and KIO_4.

Fig. 10. Calculated binding energy shifts for various free-ion states of iodine, averaged over all core levels and stated relative to the iodide ion. As abscissa we use actual ionic charge. Valence configurations are noted below the charge and are the same as those in Fig. 9.

Fig. 11. Calculated binding energy shifts due to removing a 4f electron from various free-ion configurations of europium. The configurations are: $3=4f^6$,

$2=4f^7$, $0=4f^7 6s^2$, and $1=4f^6 6s^2$. The shift values are based on our calculations. The abscissa and classical shift are analogous to those in Fig. 6. Also shown are our experimental shifts between $EuAl_2$ and Eu_2O_3.

Fig. 12. Calculated and experimental chemical shifts for iodine core levels in KIO_3 and KIO_4 with KI as a reference compound. All values are averages over the core levels. Theoretical results for both a full and three-quarter Madelung correction are given. Also shown are the points where the charge on the iodine atom is zero.

Fig. 13. Diagram illustrating the charged shell approximation as applied to an octahedral AB_6 molecule or ion with net charge m. The charge transfer due to bonding is approximated by moving charge $-e\alpha$ from the valence shell of A out to a spherical shell at radius r.

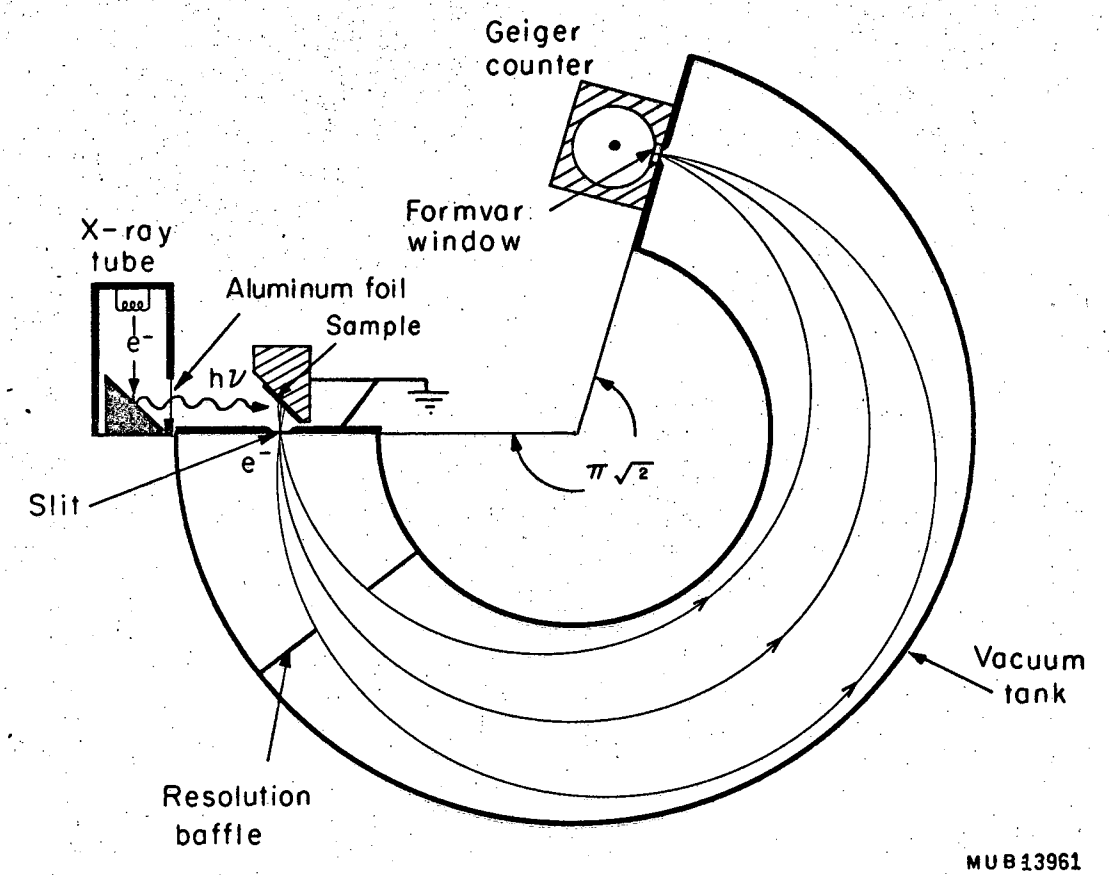

Geiger counter
Formvar window
X-ray tube
Aluminum foil
Sample
e-
hν
e-
Slit
π √2
Vacuum tank
Resolution baffle
MUB 13961

Fig. 1

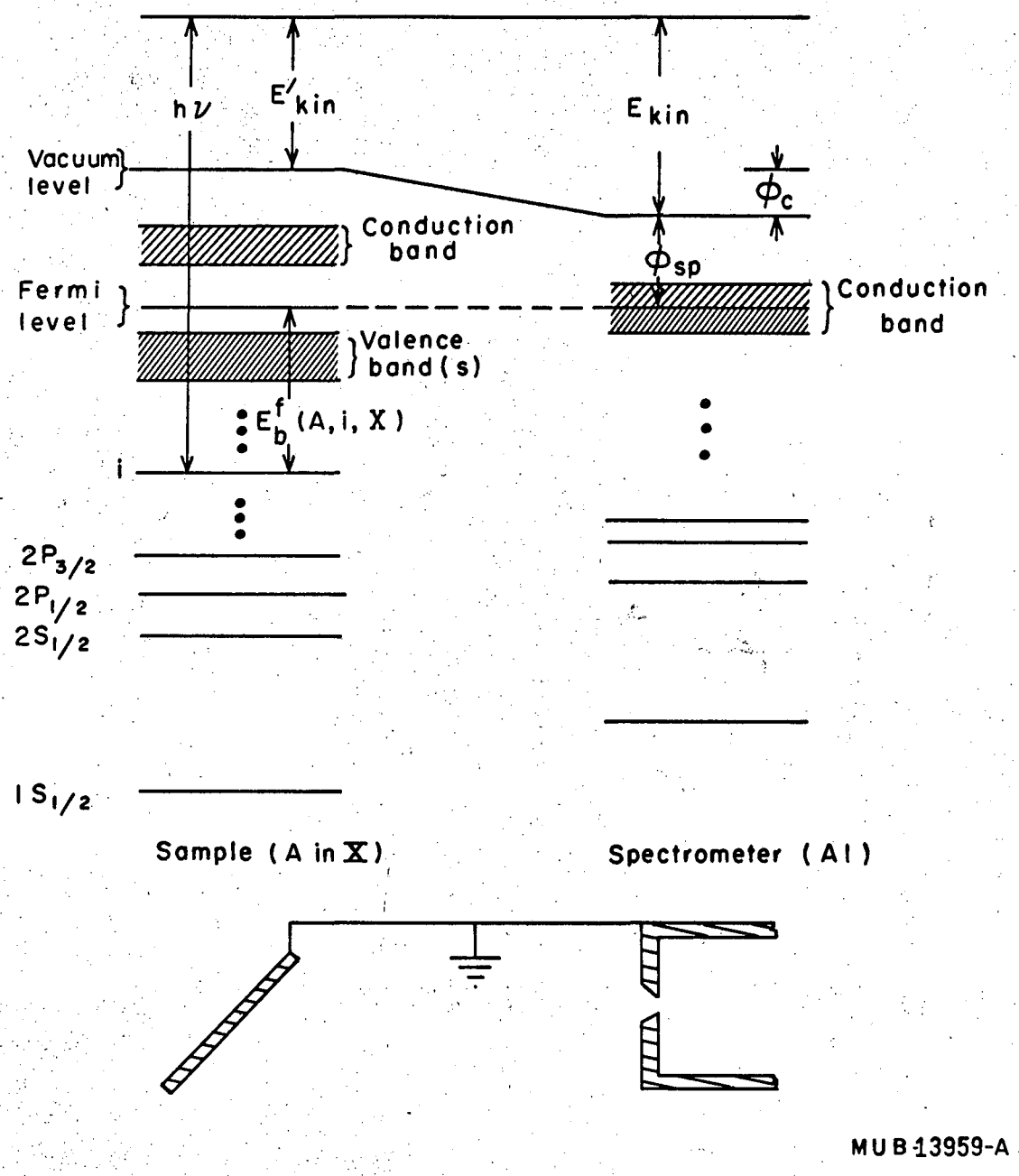
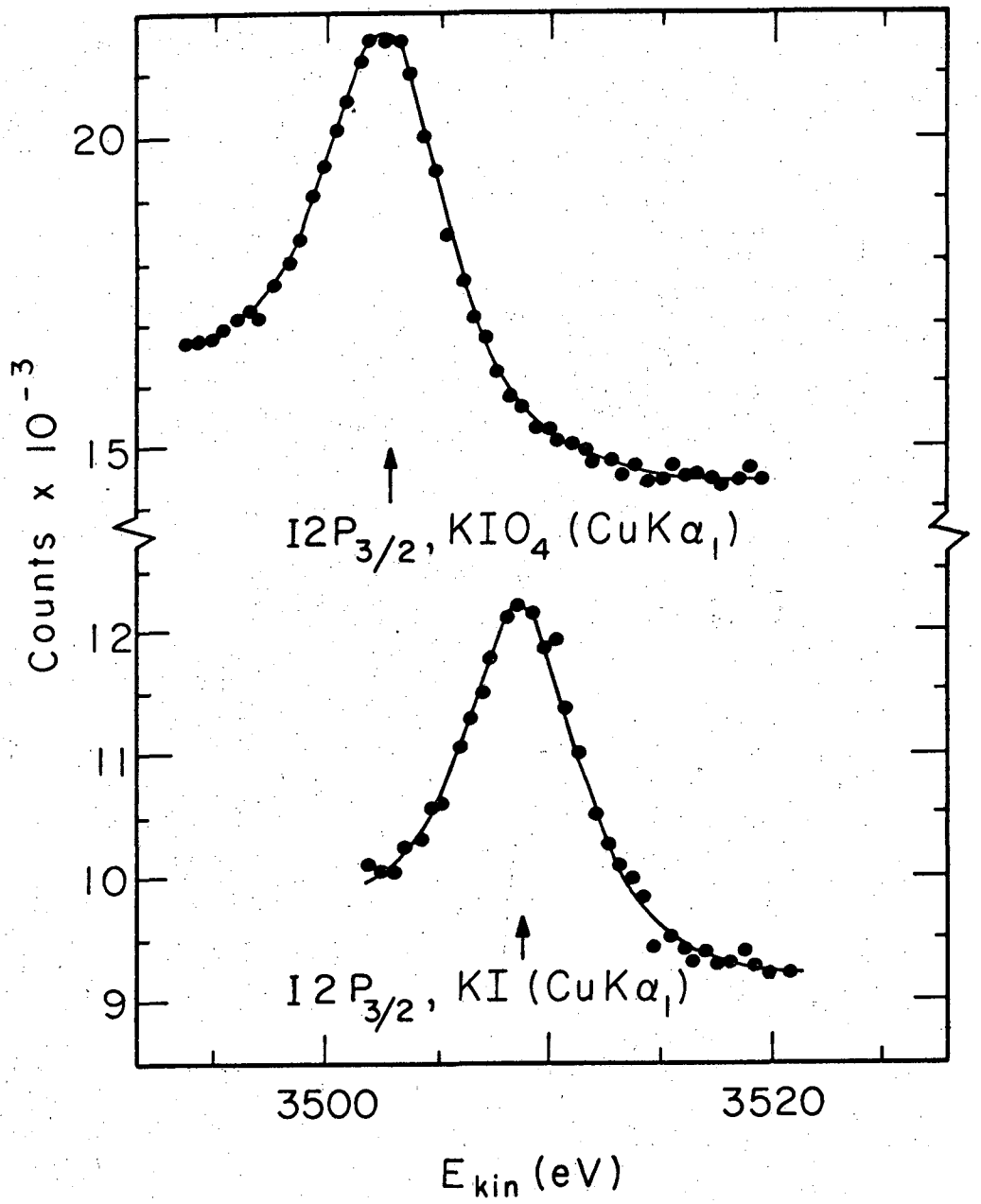

hν
E′kin
Ekin
Vacuum level
Φc
Conduction band
Φsp
Fermi level
Conduction band
Valence band (s)
E^f_b (A, i, X)
i
2P3/2
2P1/2
2S1/2
1S1/2
Sample (A in X)
Spectrometer (Al)
MUB-13959-A

Fig. 2



MUB-13960B

Fig. 3

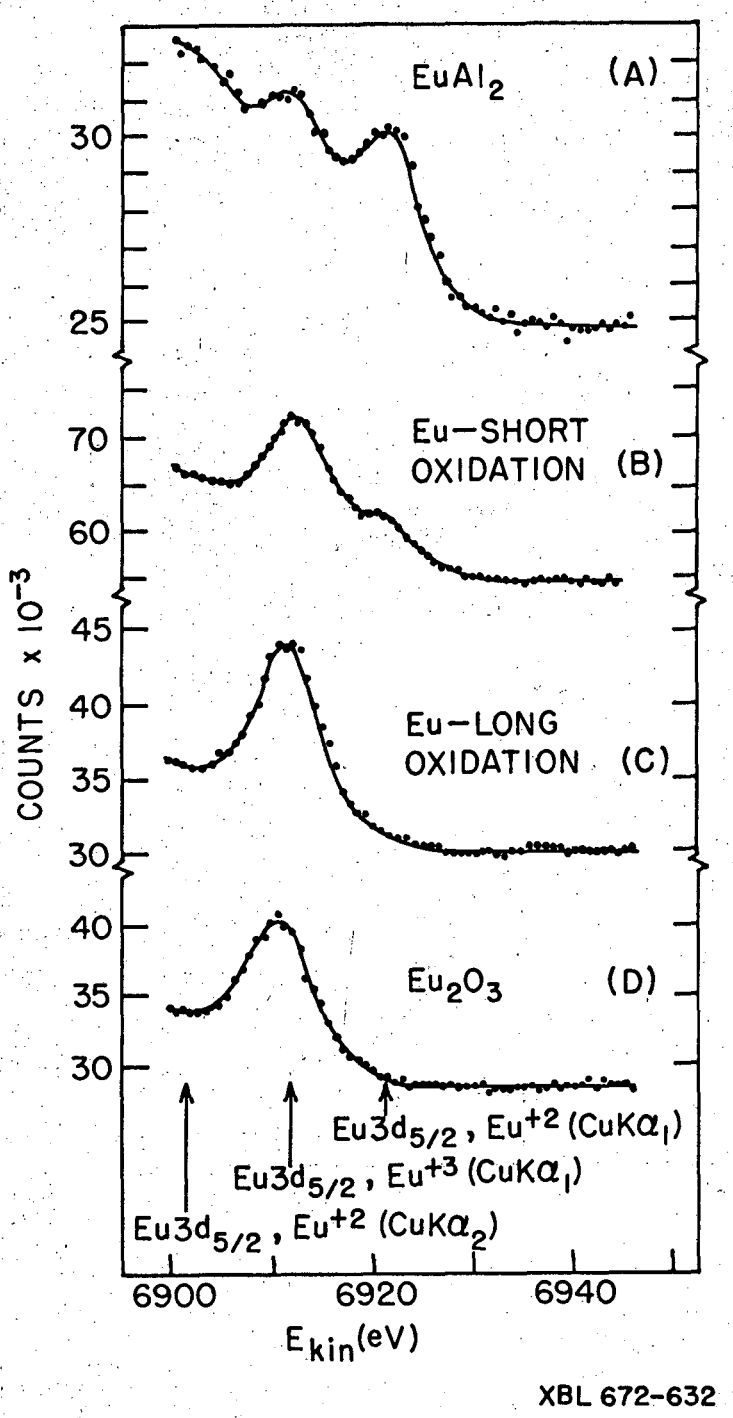

EuAl2
(A)
30
25
Eu—SHORT
OXIDATION
(B)
70
60
Eu—LONG
OXIDATION
(C)
45
40
35
30
Eu2O3
(D)
40
35
30
COUNTS x 10-3
Eu3d5/2 , Eu+2 (CuKα1)
Eu3d5/2 , Eu+3 (CuKα1)
Eu3d5/2 , Eu+2 (CuKα2)
6900
6920
6940
Ekin(eV)
XBL 672-632

Fig. 4

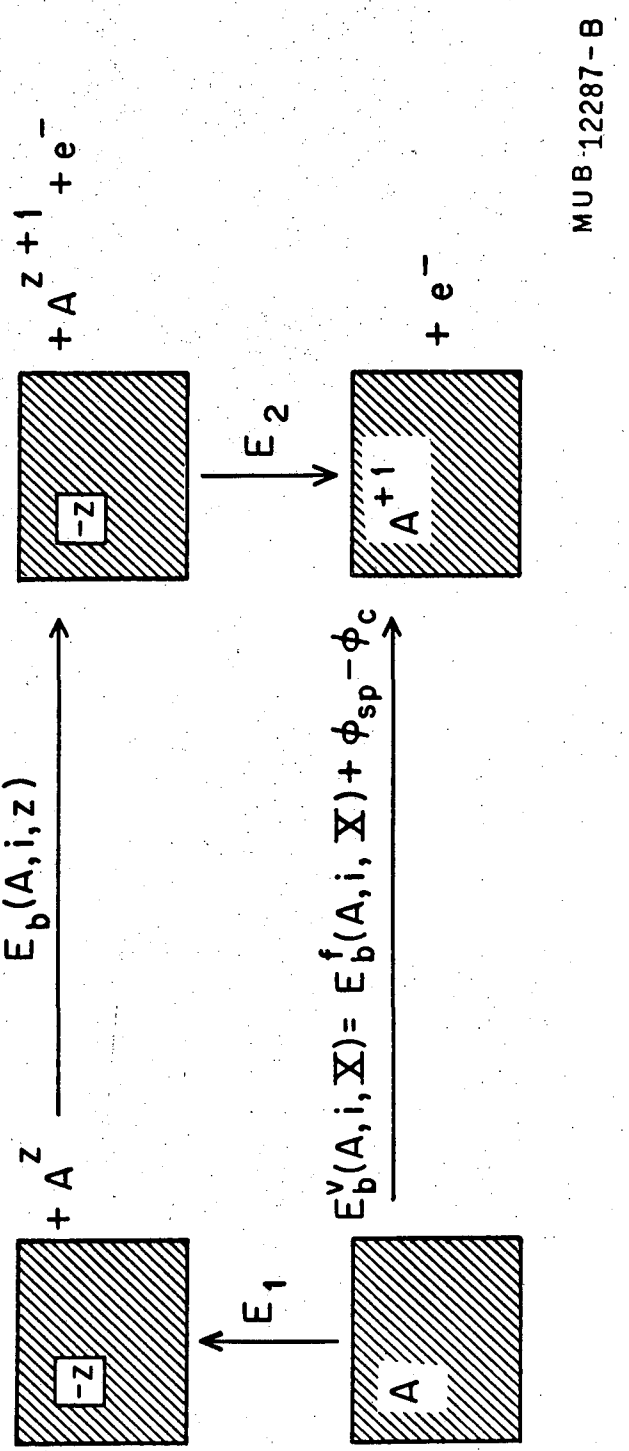
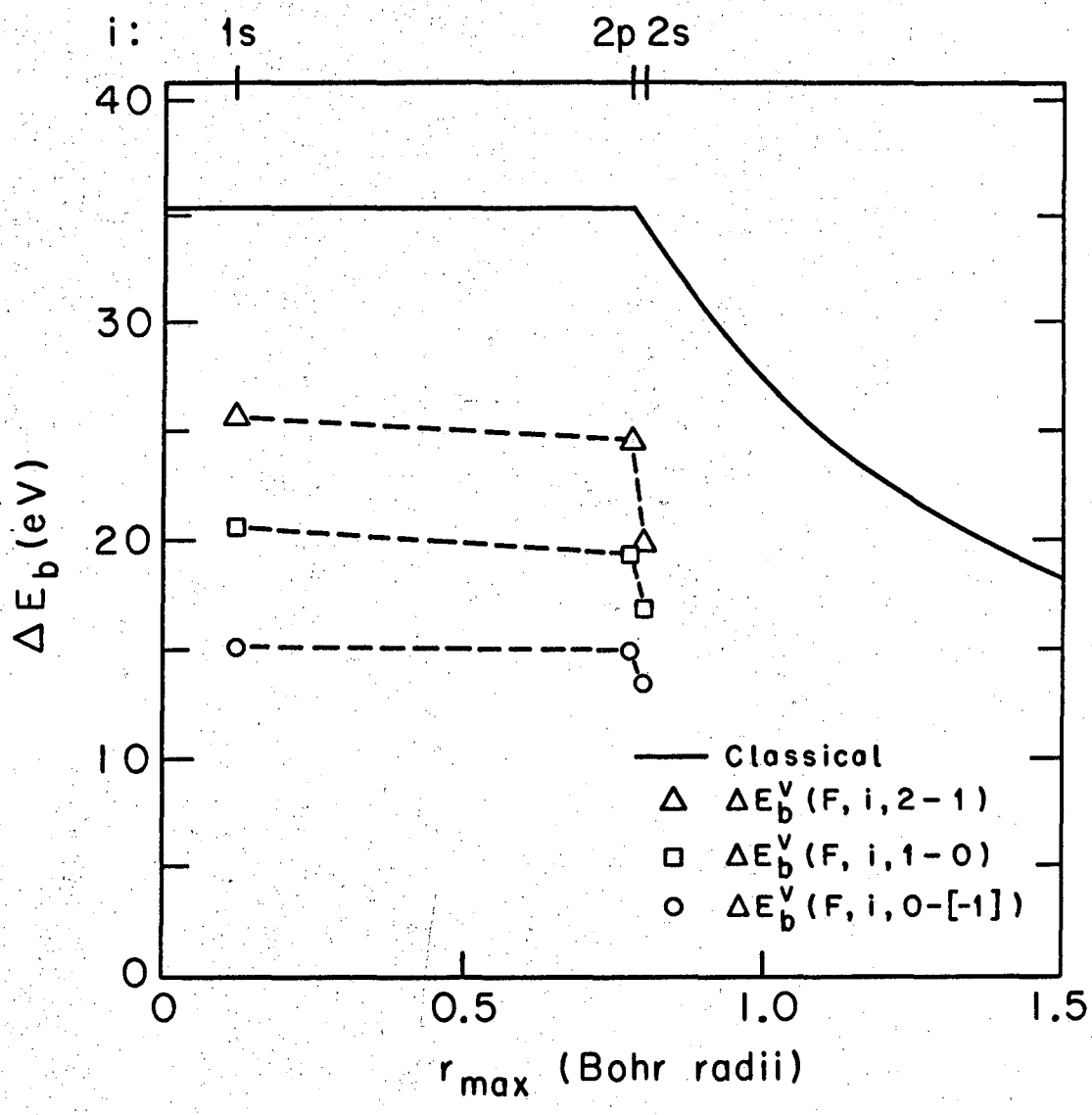
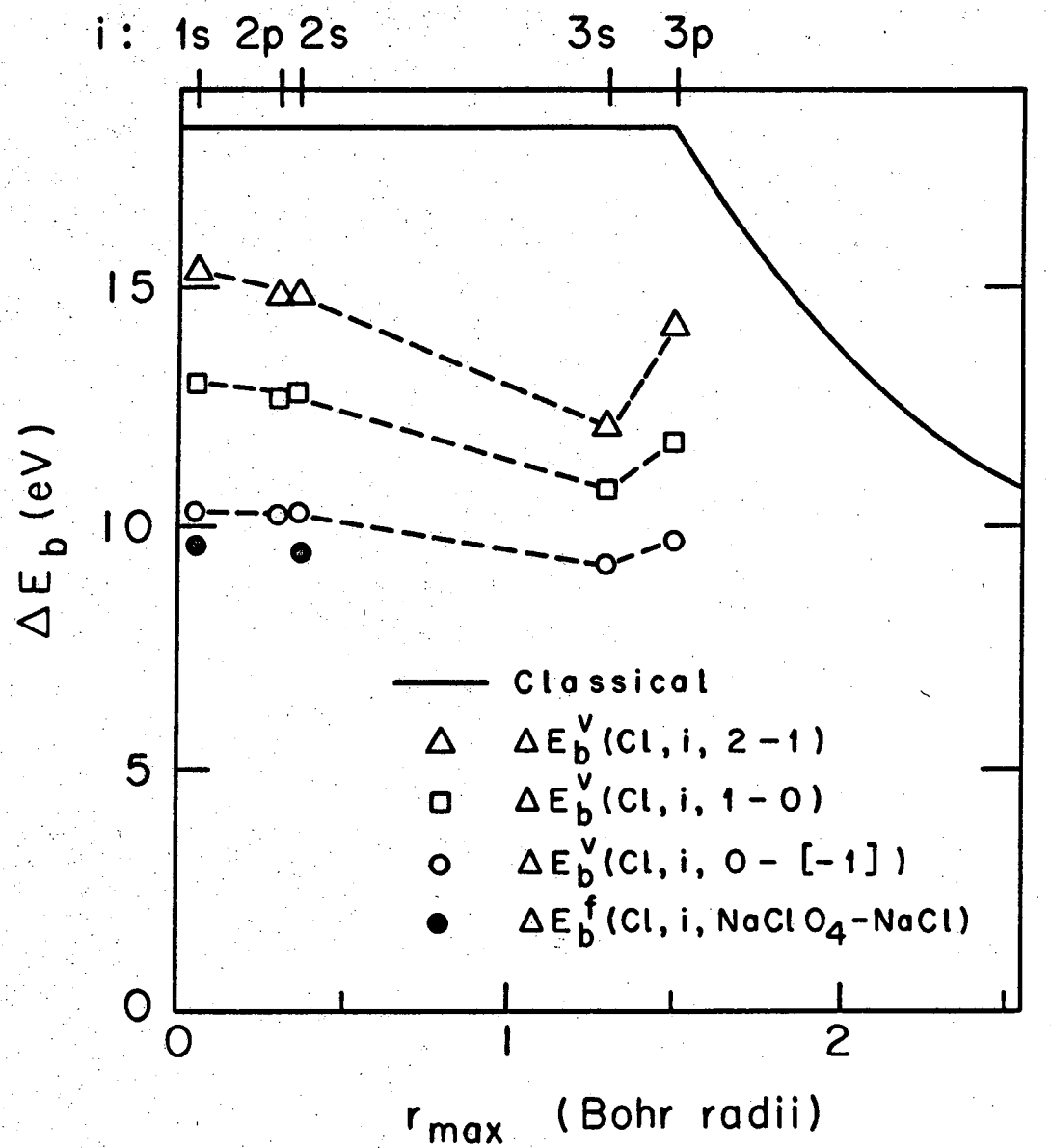

$E_b(A,i,z)$
$E_b^v(A,i,X) = E_b^f(A,i,X) + \phi_{sp} - \phi_c$
$+ A^z$
$+ A^{z+1} + e^-$
$+ e^-$
E_1
E_2
-z
-z
A
A^{+1}
MUB-12287-B

Fig. 5



XBL676-3224

Fig. 6



XBL676-3226

Fig. 7

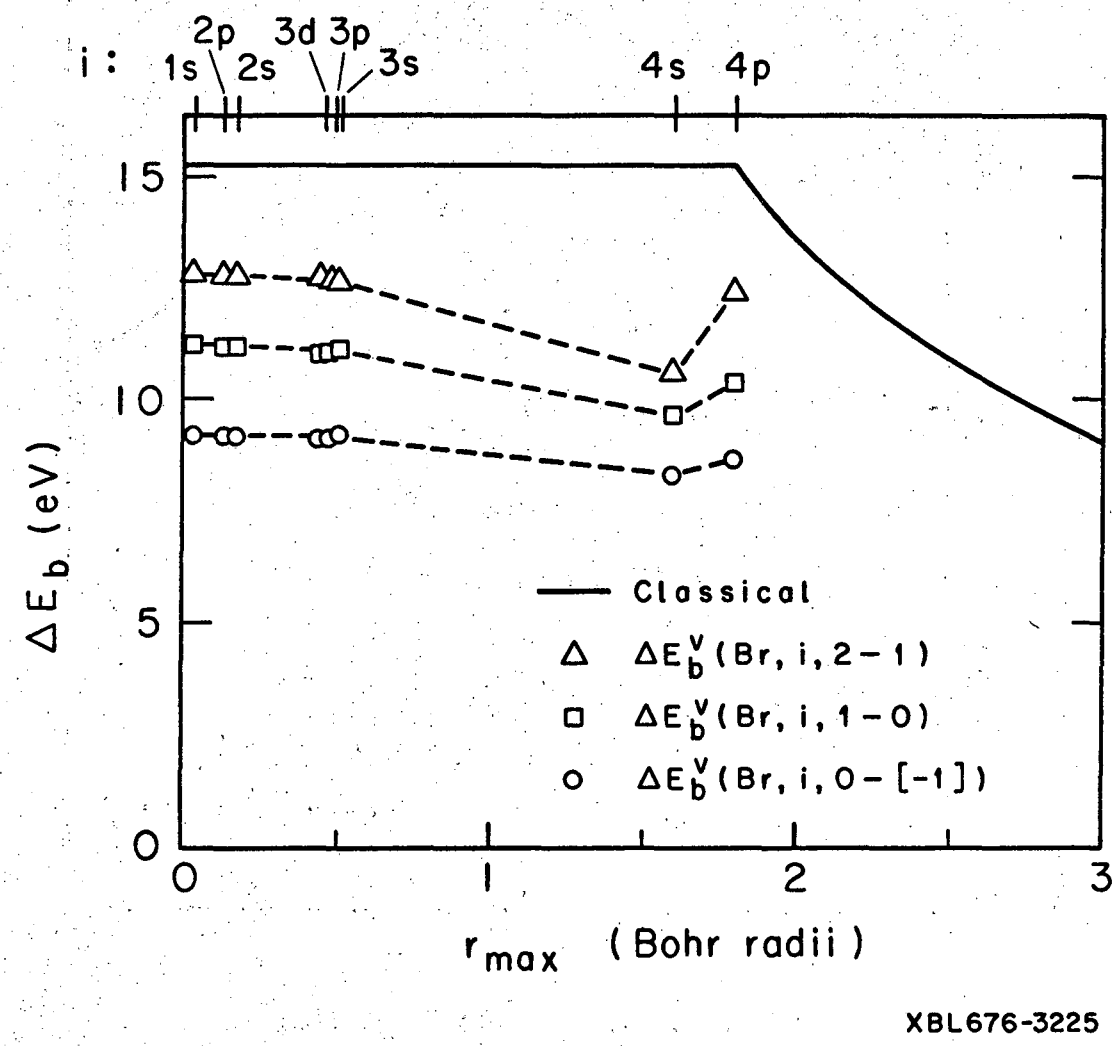
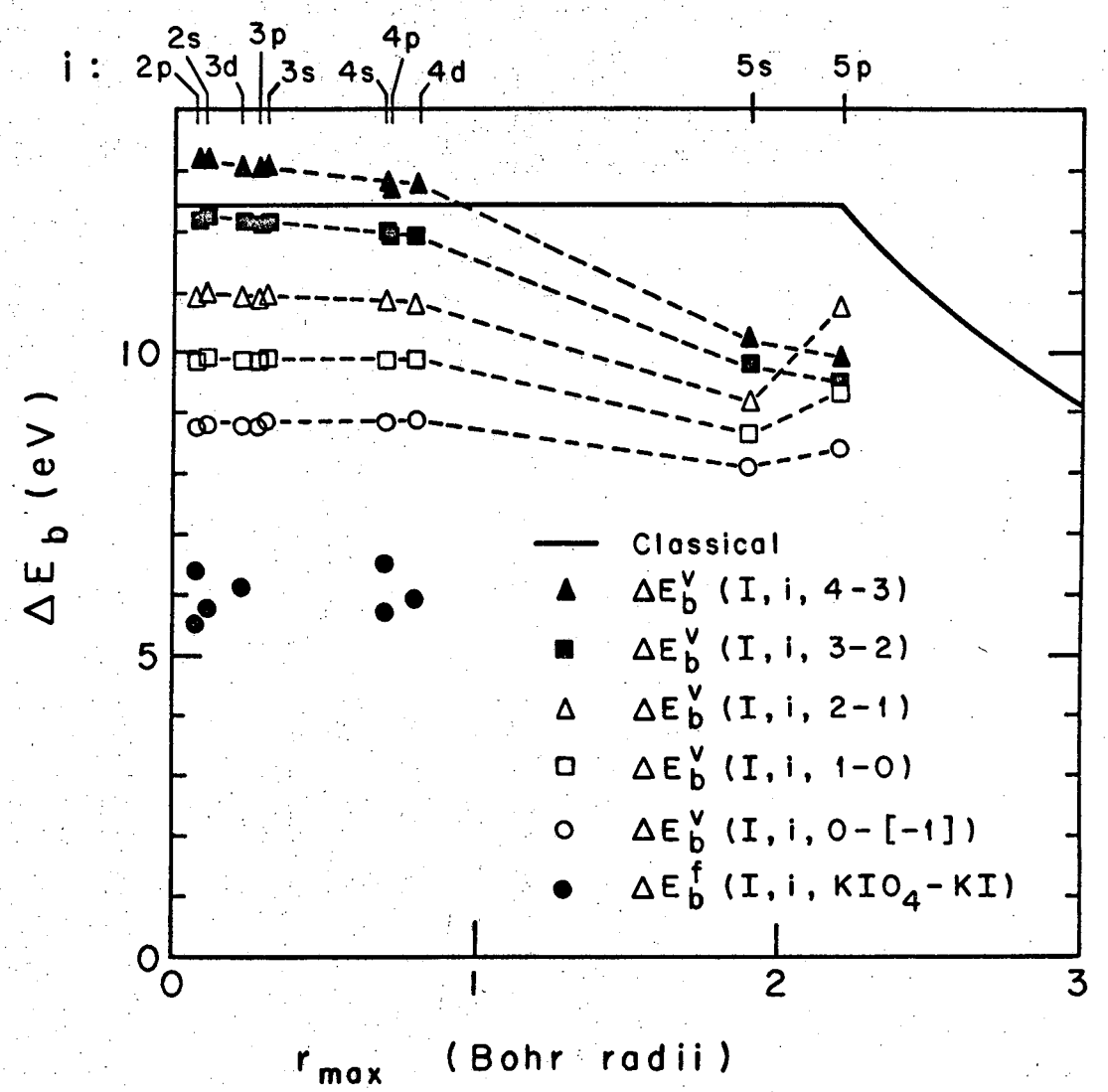
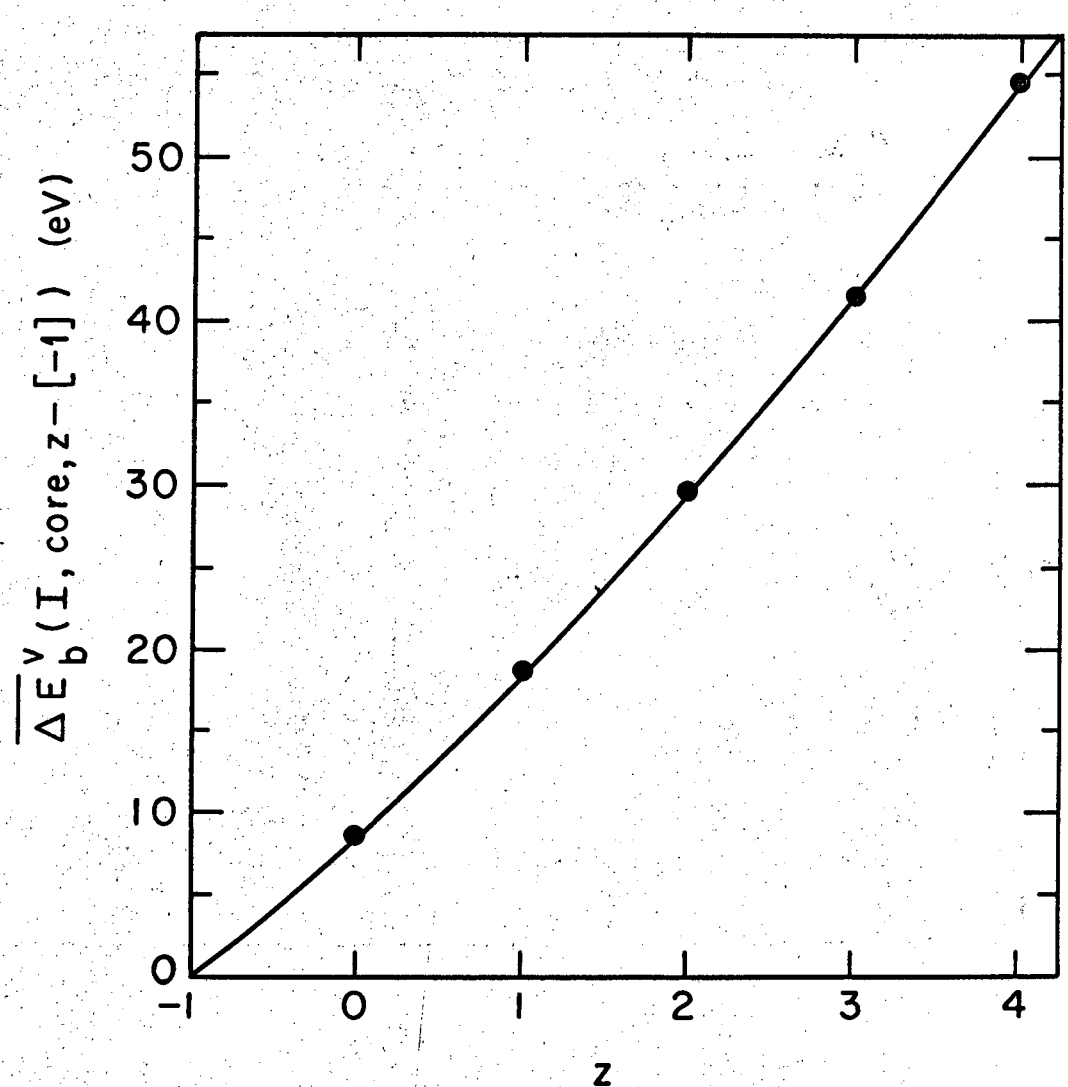

i :
1s
2p
2s
3d
3p
3s
4s
4p
15
10
5
0
ΔE_b (eV)
Classical
ΔE_b^v(Br, i, 2 − 1)
ΔE_b^v(Br, i, 1 − 0)
ΔE_b^v(Br, i, 0 − [−1])
0
1
2
3
r_{max} (Bohr radii)
XBL676-3225

Fig. 8



MUB-12292-A

Fig. 9



MUB-12286-A

Fig. 10

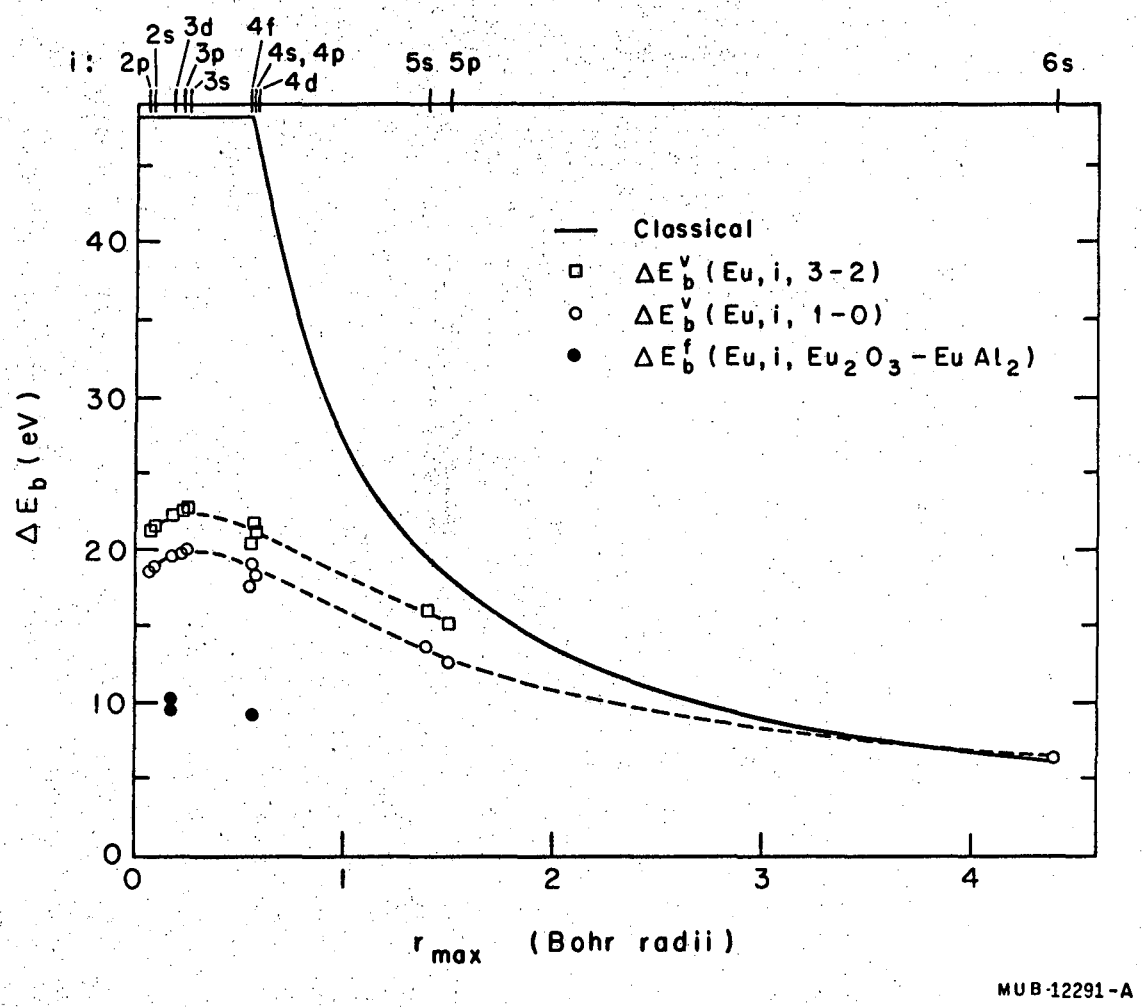
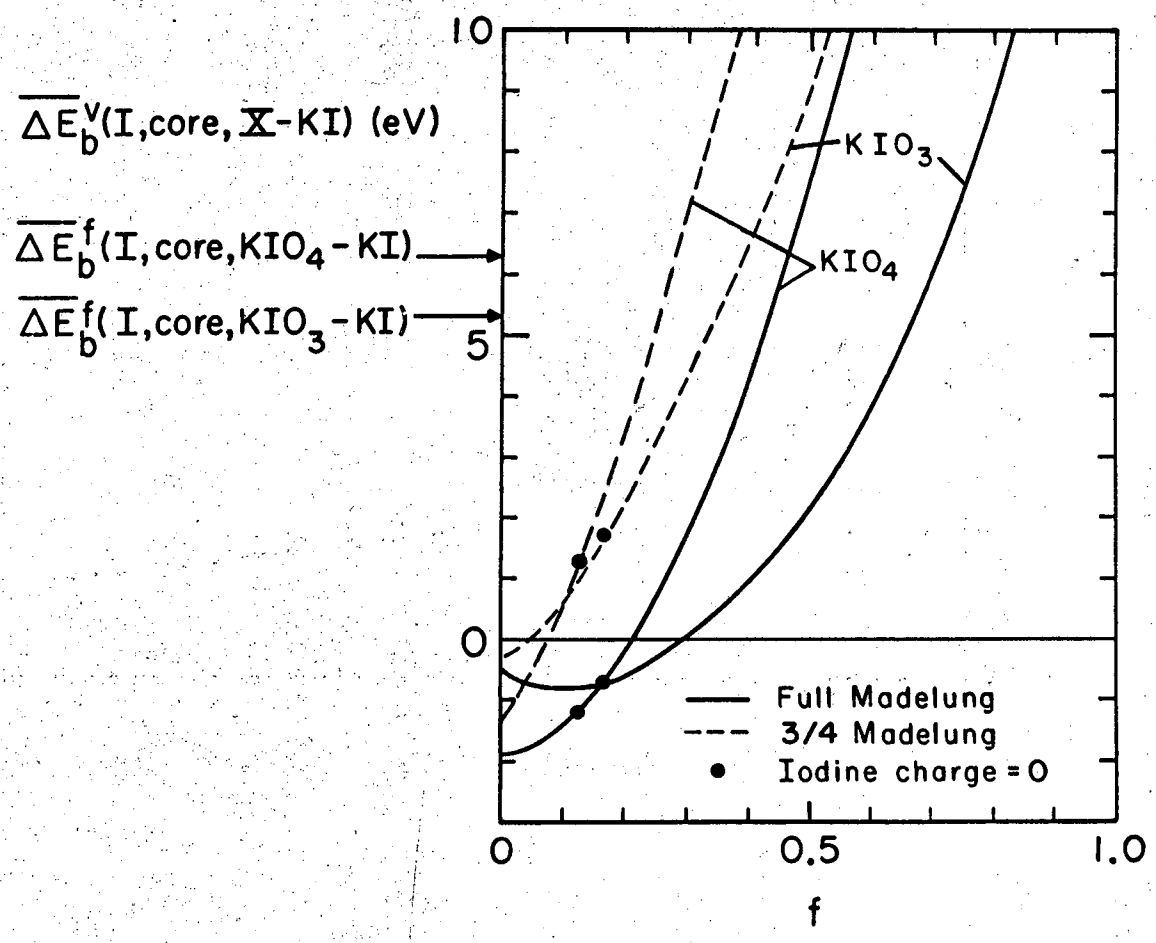
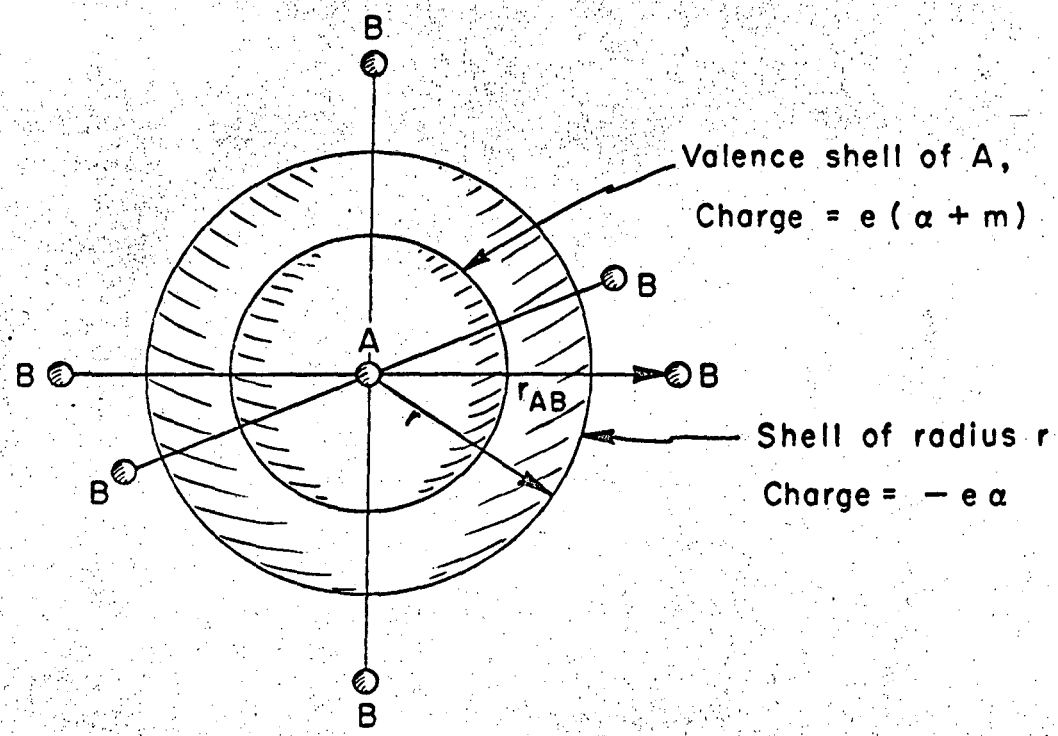

i: 2p
2s
3d
3p
3s
4f
4s, 4p
4d
5s
5p
6s
Classical
ΔE_b^v (Eu, i, 3-2)
ΔE_b^v (Eu, i, 1-0)
ΔE_b^f (Eu, i, Eu_2O_3 - $EuAl_2$)
ΔE_b (eV)
0
10
20
30
40
0
1
2
3
4
r_{max} (Bohr radii)
MUB-12291-A

Fig. 11



XBL678-3912

Fig. 12



MUB-12288-A

Fig. 13

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