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Author
Shirley, D.A.

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June 1972

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THE EFFECT OF ATOMIC AND EXTRA-ATOMIC RELAXATION
ON ATOMIC BINDING ENERGIES

D. A. Shirley
Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Abstract:

An equivalent-cores-relaxation model is given for calculating atomic binding energies from orbital energies using only ground-state atomic properties. The agreement with experiment is excellent for the noble gases. On the basis of present knowledge of atomic relaxation, the phenomenon of "extra-atomic relaxation", in which electronic charge is attracted toward a hole-state atom, is shown to have an important effect in lowering atomic core-level binding energies in condensed phases. This will affect the interpretation of most core-level binding energies measured to date.

Siegahn, et al.\textsuperscript{1, 2} have given a rather complete set of experimental electron binding energies for the chemical elements, to a precision of 1 eV or better. There exist as yet relatively few theoretical values with which these
results may be compared. This Letter describes a method for estimating atomic
core-electron binding energies from Hartree-Fock orbital energies plus a
relaxation-energy correction that employs integrals calculated from atomic
ground-state properties. The results appear to be as accurate as those obtained
from hole-state calculations, especially for heavy atoms. Comparison of experi-
mental core-level binding energies of elements with various theoretical estimates
leads to the conclusion that extra-atomic relaxation amounts to several electron
volts when measurements are made on molecules or condensed phases. Thus, except
for the noble gases, any comparisons of available experimental binding energies of
core electrons with atomic calculations should include corrections for extra-
atomic relaxation.

In seeking theoretical estimates of atomic core-level binding energies,
a good first approximation may be obtained by using the "orbital energies" from
self-consistent field (SCF) calculations. According to Koopman's Theorem,\(^3\)
the binding energy \(E_B\) of the \(i^{th}\) orbital is related to its orbital energy \(\varepsilon\) by

\[
E_B(i) \equiv \varepsilon(i) \quad .
\]  

This relation is not exact because no allowance is made for relaxation of the
passive orbitals toward the positive hole in the final state. As a result,
the measured binding energies of atomic core levels are smaller than (minus)
the corresponding orbital energies.

Bagus\(^4\) showed that SCF calculations could be carried out directly on the
final "hole" states, yielding the total energies of these states. Binding
energies could then be obtained by subtraction. Thus for the ejection of an
electron from the \(i^{th}\) orbital of an atom of atomic number \(Z\),

\[
Z + Z(i)^+ + e^- 
\]  

(2)
the binding energy is given by

\[ E_B(Z,i) = E(Z^+,\overline{i}) - E(Z) \]  \hspace{1cm} (3)

Some difficulty might be expected in calculating the hole states, because they do not rigorously satisfy the conditions required for the Variation Principle to hold. In fact, however, Bagus found satisfactory SCF solutions for the hole states, as have subsequent workers. A major drawback of this approach is that it requires a separate SCF calculation for each hole state of each element. There is not yet available even a complete set of Dirac-Fock calculations for the elements in their ground states, so a complete set of hole-state calculations (which would require over an order of magnitude more work) seems rather distant. It would be valuable to be able to estimate core-level binding energies without hole-state calculations.

Hedin and Johansson showed that the relaxation energy,

\[ E_R(i) = -\varepsilon(i) - E_B(i) \]  \hspace{1cm} (4)

can be obtained by evaluating the expectation value of a "relaxation potential",

\[ V_R = \sum_{j \neq i} (V_j^* - V_j) \]  \hspace{1cm} (5)

in the \( i \)th state. Here \( V_j \) represents the Coulomb plus exchange potential due to the \( j \)th occupied orbital and the asterisk denotes the atomic state with a hole in the \( i \)th orbital. These workers showed, specifically, that to good accuracy

\[ E_R(i) = \frac{1}{2} \langle i | V_R | i \rangle \]  \hspace{1cm} (5)
where \( \langle i | V_R | i \rangle \) is given by a linear combination of Coulomb and exchange integrals. Thus

\[
E_B = -\epsilon(i) - \frac{1}{2} \langle i | V_R | i \rangle .
\]  

(6)

Now this result still requires knowledge of \( V_j^* \), the potential due to the relaxed \( j^{th} \) passive orbital, for each value of \( j \). Exact evaluation of \( V_j^* \) would necessitate hole-state calculations, but a good approximation can be obtained by using the concept of "equivalent cores". Jolly and co-workers have used this concept to estimate binding energy shifts from ground-state thermochemical data, and recently Davis and Shirley have used it to estimate relaxation energies in molecules. The essence of this approximation is that an electron in an inner orbital will almost completely shield an outer electron from one unit of nuclear charge. An outer orbital in an atom of nuclear charge \( Z_e \) with a hole in an inner shell is therefore very closely approximated by the corresponding outer orbital in the ground state of the next element, of atomic number \( Z + 1 \). The inner orbital is contracted in element \( Z + 1 \), of course, but this has little effect on the inner electron-outer electron Coulomb and exchange integrals that are needed in Eq. (6). Thus it is a very good approximation to replace these hole-state integrals in element \( Z \) by the corresponding ground-state integrals in element \( Z + 1 \). In the notation of Slater integrals this approximation can be written as

\[
F_k(n\ell, n'\ell'; Z(n\ell)^*) \approx F_k(n\ell, n'\ell'; Z + 1)
\]

and

\[
G_k(n\ell, n'\ell'; Z(n\ell)^*) \approx G_k(n\ell, n'\ell'; Z + 1)
\]  

(7)
with \( n' > n \). Inner-shell relaxation \((n' < n)\) and intrashell relaxation \((n' = n)\), which are relatively small,\(^6\) are neglected in this approach. Slater\(^{10}\) has given expressions for the energy of interaction between electrons of angular momenta \( \ell \) and \( \ell' \). On summing over outer shells these expressions give

\[
\langle n\ell | V_R | n\ell \rangle = \sum_{\ell' \geq n} \frac{N(n'\ell')}{(4\ell' + 2)} \left\{ f(\ell\ell') \Delta \left[ F_0(n\ell, n'\ell') \right] - \Delta \sum_k \left[ g_k(\ell\ell') G_k(n\ell, n'\ell') \right] \right\}, \tag{8}
\]

where

\[
\Delta F_0(n\ell, n'\ell') \equiv F_0(n\ell, n'\ell'; Z + 1) - F_0(n\ell, n'\ell'; Z)
\]

and

\[
\Delta G_k(n\ell, n'\ell') \equiv G_k(n\ell, n'\ell'; Z + 1) - G_k(n\ell, n'\ell', Z). \tag{9}
\]

Here \( N(n'\ell') \) is the occupation number of the \( n'\ell' \) subshell in the parent atom. Thus the ratio \( N(n'\ell')/(2\ell' + 2) \) is the fractional occupation of this subshell; for a filled shell its value is unity. The factors \( f(\ell\ell') \) and \( g_k(\ell\ell') \) were obtained in an obvious way from Slater's results\(^{10}\): they are listed in Table 1.

The above approach was used to estimate relaxation energies for the noble gases Ne, Ar, Kr, and Xe, for which both usable orbital energies and experimental binding energies are available. Slater integrals were taken from the tables given by Mann.\(^{11}\) To be usable for this purpose, the orbital energies
should be obtained from SCF calculations of Hartree-Fock quality,\textsuperscript{12} and relativity should be accounted for. Rosen and Lindgren\textsuperscript{13} have described an optimized relativistic Hartree-Fock-Slater (HFS) method that yields orbital energies that are essentially identical to those obtained from relativistic Hartree-Fock calculations. They also used this optimized HFS method to obtain binding energies from hole-state calculations. The orbital energies and hole-state energies used below are their published values obtained by this optimized HFS method.\textsuperscript{1,13}

Table 2 gives the relaxation energies ($E_R$), the binding energies estimated on the theory given above ($E_B^R$), the experimental binding energies ($E_B$),\textsuperscript{1,2} and, where available, the binding energies obtained from hole-state calculations ($E_B^H$). The agreement of both $E_B^R$ and $E_B^H$ with one another and with experiment is excellent in most cases. The agreement of $E_B^R$ with $E_B^H$ shows that the "equivalent-core" potential model given here yields a very good estimate of the relaxation energy. A detailed analysis of the values of $E_R$ predicted on this model is beyond the scope of this Letter, but two observations are in order. First, the model applies only to core levels; that is, to all shells inside the outermost. Second, since no account has been taken of intrashell relaxation (which Hedin and Johansson found to be relatively small), this model is expected to, and apparently does, work best for core levels of heavy atoms.

The agreement of the $E_B^V$ values in Table 2 with experiment is actually slightly better than that of the $E_B^H$ values. This probably arises from cancellation of errors, and it may be fortuitous. Of course no final statement can be made about atomic binding energies until the effects of electron correlation have been taken into account. We note that the large discrepancies between theory and experiment for the 1s orbitals in heavy atoms arises from overlarge
values of $\epsilon(1s)$, which Rosen and Lindgren attributed to quantum electrodynamic effects.

In summary, the equivalent-core potential model yields atomic binding-energy predictions in excellent agreement with experiment, especially for heavy atoms. Of the twenty-seven measured binding energies in Table 2, 16 are within 2 eV of the $E_B^R$ predictions, and 21 are within 4 eV. In Fig. 1 the deviations of $-\epsilon$, $E_B^R$, and $E_B^H$ from the experimental values are plotted against the average radius of each orbital.

Let us now use our knowledge of atomic relaxation to address the question of possible extra-atomic relaxation effects on core-level binding energies measured in condensed phases. There exists a systematic discrepancy of nearly 10 eV between the measured 1s binding energies of the second-row elements C, N, O, and F (corrected for work function) and the atomic binding energies calculated from hole-state theory. This discrepancy is illustrated in Fig. 2, in which the difference between $E_B^H$ values from Ref. 1 and $E_B^R$ are plotted. Neon, for which a gas-phase binding energy is available,\(^3\) shows no such discrepancy. Before interpreting these results, let us review the reliability of atomic binding-energy estimates for these elements.

For free molecules containing the hydrides of C, N, or O, Schwartz\(^{14}\) gave hole-state binding energies that are within 1 eV of the experimental values. Other workers have achieved similar results in hole-state calculations of $E_B$ work for these elements in free molecules.

Let us now consider carbon specifically. The 1s binding energy in atomic carbon can be estimated in three ways. First, hole-state estimates give $E_B^H = 297$ eV. Second, the theory described above can be used to estimate
$E_R = 8.6 \text{ eV}$, which can then be combined with Mann's $-\epsilon(1s) = 308.5 \text{ eV}^{11}$ to yield $E_B^V = 300 \text{ eV}$. Finally, Siegbahn et al.\textsuperscript{2} fitted the $C(1s)$ binding energies of carbon in several small molecules to the equation $E_B = kq + V + \ell$. Setting $q$ and $V$ equal to zero, their equation would give $E_B = 291.4 \text{ eV}$ for the binding energy of a neutral carbon atom in a small molecule. Davis and Shirley\textsuperscript{8} have found that the core-hole charge of $+1$ in such a molecule is essentially completely shielded by transfer of electronic charge, through relaxation, from the ligand atoms. Assuming that the electronic charge is transferred into the $C(2p)$ shell, the extra-atomic relaxation energy can be estimated as

$$\Delta V \approx F_0(1s, 2p) - \frac{1}{6} C_1(1s, 2p) - \frac{e^2}{R} \approx 7.5 \text{ eV},$$

if the internuclear distance $R = 1.1 \text{ Å}$ of methane is used. Thus the $C(1s)$ free-atom binding energy would be about $291.4 + 7.5 = 299 \text{ eV}$. This estimate, while crude, is physically sound, and it agrees well with the above two values of $E_B(1s, \text{free atom})$. We are therefore led to the conclusion that the free-atom $C(1s)$ binding energy is in the range $297 - 300 \text{ eV}$, or very close to this range. The measured binding $C(1s)$ energy in graphite is $284 \text{ eV}$. After correction for the work function, this becomes $E_B(1s, \text{graphite}) = 288 \text{ eV}$ relative to the vacuum level. A discrepancy of about $10 \text{ eV}$ thus clearly exists for carbon. Similar considerations lead to discrepancies of about this size for the other second-row elements, as Fig. 2 indicates. We attribute this discrepancy to extra-atomic relaxation accompanying photoemission in the solid state.

Relaxation during photoemission may be understood as the natural consequence of minimizing the emitting system's Coulombic energy. In a free atom, the passive orbitals relax adiabatically, and the relaxation energy can
be estimated as discussed above. If the atom were a classical system, and charge were continuous, it would be natural to describe this relaxation in terms of the outward diffusion of a quantity of charge of value $+e$, suddenly introduced near center of the atom, in order to reduce the Coulombic repulsion energy. This picture facilitates an understanding of extranuclear relaxation molecules and solids. Thus Davis and Shirley found that the charge distribution in CH$_4^+$ immediately following emission of a C(ls) electron is approximately given by a neutral carbon atom and charges of $+e/4$ in each hydrogen, while in diatomic molecules such as CO$^+$ each atom has a charge of about $+e/2$ following ejection of a Cls electron. In fact, the ls-electron binding energies of diatomic molecules and hydrides lie between the theoretical free-atom values and the measured solid-phase values (Fig. 2), and in the order expected on the basis of extra-atomic relaxation: $E_B$(free atom) > $E_B$(diatomic) > $E_B$(hydride) > $E_B$(solid).

This order follows because a charge of about $+e/2$ is left on the host atom in a diatomic molecule, while in a hydride the positive charge can migrate to the hydrogen ligands (these two types of molecules are the simplest to consider here because in them the host atoms are nearly neutral in the initial states). In a solid sample the positive charge can migrate farther than the nearest ligand during photoemission, thereby further reducing the core-electron binding energy. This effect accounts for the reduction of $E_B$(Cls, graphite) below $E_B$(Cls,CH$_4$), for example. Similar results should obtain for other solids.

Having once established the importance of extra-atomic relaxation in relation to core-level binding energy measurements on condensed phases, we note that this phenomenon may be the key factor in understanding several previously unexplained observations. For example, core electron binding energies of
noble gases embedded in metallic foils\textsuperscript{1} were in most cases 2-5 eV higher than those of the same orbitals studied with gas-phase samples.\textsuperscript{2} Shifts of about 3 eV have also been observed in molecules between the gas and solid phase. Thus Siegbahn \textit{et al.}\textsuperscript{2} found that the Nls binding energies of aminobenzene and nitrobenzene are, respectively, 3.1 eV and 2.4 eV higher in the solid phase. This shift can be tentatively attributed to "extramolecular relaxation" due to polarization of neighboring molecules in the solid.

Extra-atomic relaxation has broad implications for all atomic binding energies obtained from data taken on solids. Because the relaxation is a property of the hole state rather than of the photoelectric process per se, it affects binding energies obtained from x-ray data, such as those tabulated by Bearden and Burr.\textsuperscript{15} It will be of interest both to estimate the corrections that must be applied to calculated free-atom binding energies before they can be compared to experiment and to measure binding energies in free atoms of more elements. As for further applications of extra-atomic relaxation, it seems probable that the relaxation energy accompanying photoemission of a core electron from an absorbed atom or molecule will depend on the nature of the substrate as well as on the nature of the binding between adsorbate and substrate. Thus extra-atomic relaxation may play a role in elucidating the adsorption process.

\textbf{FOOTNOTES AND REFERENCES}

* Work performed under the auspices of the U. S. Atomic Energy Commission.


3. T. Koopmans, Physica 1, 104 (1933).


5. Hartree-Fock orbital energies are not adequate for core levels of medium and heavy elements.


9. This statement is easily proved by the fact that the inner orbital-outer orbital Coulomb integral in a given atom differs by only a few percent from $e^2$ times the expectation value of $r^{-1}$ for the outer orbital, which is the limiting value of the Coulomb integral as the inner orbital is shrunk to a point.


12. Hartree-Fock-Slater results are not adequate, because the orbital energies do not satisfy Koopmans' Theorem. See Ref. 13.


Table 1. The f and g Coefficients in Eq. (9)

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Table 2. Noble Gas Core-Electron Binding Energies (eV)

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<td>Xe 4d_{5/2}</td>
<td></td>
<td></td>
<td>66.2</td>
<td>67.5</td>
</tr>
</tbody>
</table>

(continued)
Table 2. (continued)

<table>
<thead>
<tr>
<th>Estimate</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Estimated using Eqs. (5) - (9), and integrals from Ref. 11.</td>
</tr>
<tr>
<td>b</td>
<td>From Refs. 1 and 13.</td>
</tr>
<tr>
<td>c</td>
<td>The orbital energies for these estimates were taken from Refs. 1 and 13.</td>
</tr>
<tr>
<td>d</td>
<td>From Refs. 1 and 2.</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Plots of the deviations of theoretical binding energies from experiment four rare gases, using orbital energies (Δ), hole-state energies ( ), and the method described herein (O). The abcissa is the orbital radius in atomic units. The Xe ls values are not shown.

Fig. 2. The binding-energy discrepancy for ls orbitals of second-row elements in solids. Filled circles represent $E_B^H_{\text{atomic}} - E_B^{\text{expt.}}$. Only the neon point is a gas-phase result. Triangles and squares show excess binding energies (over the experimental values in solids) for gaseous diatomics and hydrides, respectively.
Fig. 2

Excess binding energy (eV) vs. Atomic number

C N O F Ne

Excess binding energy shown for C, N, O, F, and Ne.
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