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THE PREDICTION OF CORE-LEVEL BINDING-ENERGY SHIFTS FROM CNDO MOLECULAR ORBITALS*

D. W. DAVIS and D. A. SHIRLEY

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 (U.S.A.)

ABSTRACT

A theory is described for calculating core-level binding-energy shifts with potential models that employ "intermediate-level" molecular-orbital wavefunctions. The relaxation-energy term in atomic core-level binding energies is considered first. The ground-state potential model (GPM) and relaxation-potential model (RPM) are developed for calculating core-level binding energy shifts in molecules from CNDO wavefunctions. It is shown that neglect of certain two- and three-center integrals in these models limits their accuracy when unlike molecules are compared. The models are modified by calculating $\langle r^{-1} \rangle$ integrals, to be sensitive to bond directions of p orbitals. The pp' modification, in which a subset of the neglected integrals is retained to recover invariance to coordinate transformations, is thereby necessitated. The GPM approach yields shifts in very good agreement with experiment when comparisons are restricted to similar molecules. The RPM version gives better agreement especially over wider classes of molecules. It also provides relaxation energies V_R that can be combined with <u>ab initio</u> orbital energies to give binding energies. Several applications of these potential models are discussed.

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INTRODUCTION

Chemical shifts in core-level binding energies (ESCA shifts) have received a great deal of attention recently[1]. Many workers have independently contributed theoretical insights into the origin of these shifts. It is now clear both that the shifts can be rather well understood at several levels of mathematical sophistication and that they are quite useful in interpreting chemical properties. As yet, however, the theoretical literature is rather fragmentary, with each contribution tending to emphasize a single aspect of the theory of core-level binding-energy shifts. The purpose of this paper is to develop part of the theory systematically in a way that will interrelate the several approximations that are commonly made in interpreting ESCA shifts. We do not presume to give a rigorous presentation. Instead, we aim rather directly toward simple models that any chemist can use to interpret shifts in terms of chemically useful concepts such as charge distributions in molecules. It is our hope that this paper will serve both as a badly-needed introduction to the theory and as a useful guide for anyone who wishes to use core level shifts for chemical purposes.

The format of this paper is the development of core-level shift theory in atoms and molecules from the basic photoemission relation $K = h\nu + E_i - E_f$ through several approximations to the potential models that can be used directly in "atomic-charge" analyses, in which the charge distributions in molecules are derived from core-level shifts. Many theoretical subleties are omitted, but the physical significance of the important approximations is discussed. There is, in our opinion, a rather exclusive relationship between the rigor of a given approach to binding-energy shift theory and the breadth of applicability of that approach. It is important to establish whether in this

hierarchy of theories there exists a range wherein the theories are both tractable, in the sense of being readily usable by anyone measuring shifts, and also sufficiently reliable and quantitative to yield really incisive chemical information. We believe that such a range does exist and that "intermediate level" molecular-orbital theories such as CNDO lie in this range. This is a central theme of the paper, and much of the early development is aimed toward the goal of applying CNDO theory to core-level shifts.

Core-hole states and the relaxation energy in atoms are discussed in the next section. A method is given for approximating the relaxation energy in atoms. Potential models are introduced in the following section and the GPM (ground state potential) approximation is developed. The relaxation potential model (RPM) is then discussed. Typical applications and a summary of the model are given in the last section.

CORE HOLE STATES AND APPROXIMATIONS

In the x-ray photoemission of a core electron from orbital k of a molecule M, the simplest process that can occur is a transition to an ion $M(\bar{k})^+$ in a "relaxed" core hole final state:

$$\text{photon} + M \rightarrow M(\bar{k})^+ + e^- \quad . \tag{1}$$

Here the ion $M(\bar{k})^+$ differs from the molecule M in two ways: an electron is missing from orbital k, and the passive orbitals have relaxed adiabatically to adjust to this modification in the molecular potential. Other processes are also possible. These include the "shake-up" and "shake-off" transitions, in which (respectively) more highly excited or doubly ionized final states

are reached, with the additional excitation energy being deducted from the photoelectron's kinetic energy:

$$\text{photon} + M \rightarrow M(\bar{k})^{+*} + e^- \qquad \text{(shake-up)} \tag{2a}$$

$$\text{photon} + M \rightarrow M(\bar{k}\bar{\ell})^{++} + 2e^- \quad . \quad \text{(shake-off)} \tag{2b}$$

These processes can appear as satellites, at lower kinetic energies, on the main photoemission line arising from the process in Equation (1). We will not discuss these two-electron processes but will be concerned only with the photoemission channel that reaches the relaxed core-hole final state.

In considering the relaxation accompanying photoemission it is useful to define a hypothetical "unrelaxed" ionic final state $|M(\bar{k})^+_{KT}\rangle$ in which an electron has been removed from the core level k of the molecule M <u>without</u> any relaxation in the passive orbitals. This state does not exist in nature. Its virtue is that, according to Koopmans' Theorem[2] the binding energy for the hypothetical process

$$M \rightarrow M(\bar{k})^+_{KT} + e^- \quad , \tag{3}$$

is exactly $-\varepsilon(k)$, where $\varepsilon(k)$ is the orbital energy of the orbital k that would be obtained from a Hartree-Fock calculation on M. Manne and Åberg showed[3] that the binding energy E_B in the Hartree-Fock approximation is related to ε by a sum rule

$$-\varepsilon(k) = E_B(k) + \sum_i |\langle M_i^* | M(\bar{k})^+_{KT}\rangle|^2 \, (E_B^i - E_B(k)) \quad , \tag{4}$$

where the sum is taken over all the excited states i in the photoelectron spectrum. Thus the "orbital" binding energy $-\varepsilon$ is the weighted average energy for these excited states plus the relaxed final state $M(\bar{k})^+$. Since $E_B^i > E_B(k)$ for all i, it follows that $-\varepsilon > E_B(k)$. This is of course expected, as relaxation of the passive orbitals toward the hole should lower the energy.

Binding energies are calculated in two ways. The first is suggested by Equation (1). The corresponding energy-balance equation can be rearranged to

$$h\nu - K = E[M(\bar{k})^+] - E(M) \equiv E_B(k) \quad , \tag{5}$$

where K is the photoelectron's kinetic energy. This equation suggests that $E_B(k)$ could be obtained as the difference between the calculated total energy of the initial state, $E(M)$ and that of the final state, $E[M(\bar{k})^+]$. Although there are some problems associated with using variational methods on such highly-excited states, this approach works rather well in practice. Bagus demonstrated its applicability for calculating binding energies of core levels in atoms[4], and Schwartz extended it to molecules[5]. Recently Moser, et al.[6] have refined this method to include correlation and have obtained excellent agreement with experiment for the Ne(1s) binding energy. While this approach is thus capable of yielding accurate results for small systems, the feasibility of applying it to even medium-sized molecules is clearly limited at this time, and we shall not discuss it further.

The second way of calculating binding energies is to start from the orbital energy $-\varepsilon$ and correct for the relaxation energy E_R of the passive orbitals,

$$E_B = -\varepsilon - E_R \quad . \tag{6}$$

This method has an advantage in principle (provided that E_R can somehow be estimated with reasonable accuracy) because a single SCF calculation of the molecular ground state yields orbital energies ε for all the one-electron orbitals of the molecule. Hedin and Johansson[7] have shown how this approach is related to direct hole-state calculations. They found

$$E_R^{(i)} = \frac{1}{2}\langle i|V^* - V|i\rangle \quad , \tag{7}$$

to a good approximation, where $E_R^{(i)}$ is the relaxation energy accompanying photoemission from orbital $|i\rangle$, while V^* and V are respectively the "Fock potential" operators for the ith orbital in the relaxed hole state and in the ground state. Specifically,

$$\langle i|V|i\rangle = \sum_j (2J_{ij} - K_{ij}) = e^2 \sum_j \Big\{ 2\langle i(\mu)\ j(\nu)|r_{\mu\nu}^{-1}|i(\mu)\ j(\nu)\rangle - \langle i(\mu)\ j(\nu)|r_{\mu\nu}^{-1}|i(\nu)\ j(\mu)\rangle \Big\} \quad , \tag{8}$$

where J_{ij} and K_{ij} are two-electron Coulomb and exchange integrals, $r_{\mu\nu}$ is an interelectronic distance, $i(\mu)$ means electron μ in orbital i, etc., and the sum is taken over all occupied orbitals j. The physical meaning of Equations (7) and (8) is that the passive orbitals j collapse adiabatically "toward" the hole in the active orbital i during photoemission. Since each orbital j changes slightly, the relaxation energy is made up of differences between Coulomb and exchange integrals before and after relaxation,

$$\Delta J_{ij} = J^*_{ij} - J_{ij}$$

$$\Delta K_{ij} = K^*_{ij} - K_{ij} \quad . \tag{9}$$

Equations (7-9) are useful in understanding the origin of the relaxation energy, but they offer no immediate advantage in calculating binding energies, because they require hole-state wavefunctions. If one is going to carry out hole-state calculations, one may as well deduce E_B from the total energies. However, the Hedin-Johansson model is a very useful starting point for further approximations, as discussed below.

In free atoms, relaxation toward holes can be treated in three parts. If the hole is in the shell with principal quantum number n, there is "inner-shell relaxation", by electrons in orbitals with $n' < n$, "intrashell relaxation", $n' = n$, and "outer shell relaxation", $n' > n$. Hedin and Johansson found that inner-shell relaxation is relatively very small ($\sim 10^{-2}$ eV). Intra-shell relaxation is somewhat larger. Outer-shell relaxation is by far the largest of the three in true core levels, for which there are a reasonably large number of electrons present in outer shells, with $n' > n$. This term can also be quite accurately estimated by a simple model[8] that employs only ground-state two-electron atomic integrals, which have been calculated by Mann[9]. In this model it is recognized that electrons in the n shell shield electrons in the $n' > n$ shell from the nucleus very effectively. Thus the adiabatically relaxed n' orbital in a hole state ion $A(Z,\bar{n})^+$ is well simulated by the n' orbital in the ground state of the atom of next highest atomic number, $A(Z + 1)$. The quantities required in Equation (9) are therefore approximated by

$$\Delta J_{ij}(Z) \cong J_{ij}(Z + 1) - J_{ij}(Z)$$

$$\Delta K_{ij}(Z) \cong K_{ij}(Z + 1) - K_{ij}(Z) \quad . \tag{10}$$

Two objections to this approach may be made. First, the shielding of the n' shell by the n shell is presumably not complete. Second, the n orbital is different in the hole state ion $A(Z,\bar{n})^+$ than in the atom $A(Z + 1)$; this affects the two-electron integrals. The first objection is partially answered by the success of this "equivalent cores" approach in predicting binding energies[8]. It is discussed further below. The second objection is easily answered. It turns out that the extra-atomic contribution to E_R is very insensitive to the form of the hole-state orbital. This is convincingly demonstrated by comparing the values of

$$\Delta \langle \frac{1}{r_{n'}} \rangle = \langle \frac{1}{r_{n'}} \rangle_{Z+1} - \langle \frac{1}{r} \rangle_{Z}$$

and

$$\Delta F^0(nn') = F^0(nn',Z + 1) - F^0(nn',Z) \quad . \tag{11}$$

The reason for this comparison is that the Slater integral F^0 accounts for almost all (> 95%) of the outer-shell relaxation energy. If the orbital n is shrunk to a point at the nucleus, we have

$$\lim_{n \to \text{point}} F^0(nn') = \langle \frac{1}{r_{n'}} \rangle \quad . \tag{12}$$

Thus a comparison of $\Delta \langle 1/r_{n'} \rangle$ and $\Delta F^0(nn')$ gives an indication of how much E_R would change if orbital n were altered in this drastic way. We have made

such a comparison for a number of cases. The results for argon, which are typical, are summarized in Table 1. In addition to estimates of E_R for the 1s, 2s, and 2p electrons from $\Delta \langle 1/r_{n'} \rangle$, and $\Delta F^0(nn')$--the two quantities that are directly comparable--we have also listed estimates from the full "equivalent cores" treatment[8], labeled $\Delta(F,G)$, from Hartree-Fock hole-state calculations, from optimized Hartree-Fock-Slater (OHFS) hole-state calculations[10], and from "experiment"; i.e., from a comparison of experimental binding energies[11] with orbital energies from OHFS calculations[12]. The $\langle r^{-1} \rangle$ values used for Table 1 were obtained from Mann's Hartree-Fock calculations[13]. Since the estimates of E_R from $\Delta \langle 1/r_{n'} \rangle$, corresponding to orbital n being shrunk all the way to a point, differs by only 2 eV from ΔF^0, we conclude that E_R is quite insensitive to small changes in this orbital. Thus we need not be concerned by the second objection given above to the use of Equation (10). Incidentally, the comparison in Table 1 (and others that we have made) shows only that total <u>changes</u> in $\langle 1/r \rangle$ and F^0 from Z to Z + 1 are similar. The actual <u>values</u> of $\langle 1/r \rangle$ and F^0 can differ by larger amounts.

The equivalent-cores model appears to estimate binding energies of true core levels as accurately as do the OHFS calculations, judged by comparison with the available data. Comparisons with rare-gas data[8] showed this to be true for Ar, Kr, and Xe. Since then core-level binding energies for the $4f_{7/2}$ states in gaseous Pb and Bi have become available[14]. Table 2 compares these results with theoretical estimates based on the equivalent-core model[8]. The very good agreement again supports the use of this approximate model for core levels. We conclude that the equivalent-cores approach provides good estimates of the total relaxation energy for core levels, although it only explicitly

TABLE 1

RELAXATION ENERGIES IN ARGON (IN eV)

Orbital	E_R from					
	$\Delta\langle 1/r_{n'}\rangle$ [a]	ΔF^0 [b]	$\Delta(F,G)$ [c]	HF [d]	OHFS [e]	"Expt." [f]
1s	40.0	38.1	37.0	32.2	31.8	34.1(7)
2s	13.3	11.1	10.5	10.4	9.9	9.7(5)
2p	13.3	11.3	11.1	11.5	11.1	10.5(5)

[a] Using $\langle r^{-1}\rangle$ values from ref. 13.

[b] Using F^0 values from ref. 9.

[c] See ref. 8.

[d] From ref. 4.

[e] From ref. 10.

[f] $E_R = -\varepsilon$ (ref. 12) $- E_B$ (ref. 11).

TABLE 2

THE $4f_{7/2}$ BINDING ENERGIES IN ATOMIC Pb AND Bi (IN MeV)

Level	$-\varepsilon^{a}$	E_R^{b}	E_B(theo)	E_B(expt)
Pb($4f_{7/2}$)	154	11	143	144.0(5)
Bi($4f_{7/2}$)	175	11	164	164.9(5)

[a]Ref. 12. The Pb value was interpolated.

[b]Calculated as in ref. 8.

[c]Ref. 14.

considers outer-shell relaxation. In fact it is not clear why these estimates are so accurate. Omission of intra-shell relaxation may be compensated in part in this approach by systematic over-estimation of the outer-shell contribution. This point is illustrated in Table 3, in which the contributions of various shells to the relaxation energies of the 1s, 2s, and 2p holes in atomic potassium, calculated both for hole states[7] and by the equivalent-cores approach[8], are compared. Since the latter model makes no allowance for intra-shell relaxation, it is suitable only for core states. If the equivalent-cores model for relaxation works this well in atoms it should certainly be valid in molecules, because the additional (extra-atomic) electrons are further removed from the active core. Thus in the next section we shall use it with confidence in connection with chemical shifts and relaxation in molecules.

CHEMICAL SHIFTS AND THE GROUND-STATE POTENTIAL MODEL (GPM)

In progressing from atoms to molecules we encounter qualitatively more difficult problems in calculating core-level binding energies. From a purely computational point of view the straightforward approach of taking total energy differences quickly becomes impractical as molecules become larger, and it is necessary to seek viable approximations. In doing so it is very important to remember the physical principles that emerged in considering the binding energies of core levels in atoms. One could regard those binding energies as being affected by two factors: the electrostatic potential energy V experienced by the core electron in the ground state before ionization, and a relaxation potential energy $V^* - V$ (Equation (7)) that arises from redistribution of electronic charge during ionization. Both of these factors are more complex in molecules

TABLE 3

CONTRIBUTIONS OF INDIVIDUAL SHELLS TO HOLE-STATE RELAXATION ENERGY IN POTASSIUM (eV)

Passive Orbitals	Active Orbital					
	1s[a]	1s[b]	2s[a]	2s[b]	2p[a]	2p[b]
1s	1.43	--	0.00	--	0.01	--
2s	3.17	5.31	0.26	--	0.52	--
2p	15.32	18.99	1.73	--	2.24	--
3s	2.27	2.77	1.40	2.33	1.58	2.36
3p	9.39	9.51	6.30	8.10	6.65	8.30
4s	1.25	0.84	1.13	0.80	1.18	0.81
Total	32.83	37.42	10.82	11.23	12.18	11.47

[a]From ref. 7.

[b]Calculated as in ref. 8.

than in atoms. Consideration of only the first factor leads with several approximations to formulation of a ground-state potential model (GPM), discussed below, that appears to be quite reliable in predicting binding-energy shifts among restricted sets of molecules. If both factors are considered, the same approximations yield a relaxation potential model (RPM), which is treated in Section IV.

The ground-state electrostatic potential affects the binding energy of a core level $|i\rangle$ directly through the orbital energy

$$\varepsilon_i = \varepsilon_i^0 + \sum_j (2J_{ij} - K_{ij}) \quad . \tag{13}$$

Here the one-electron energy ε_i^0 is the expectation value of the operator

$$-\frac{1}{2}\nabla^2 - \sum_{\text{nuclei}} Z_n/r_n \quad .$$

In an atomic system there is only one nucleus and ε_i^0 can be regarded as essentially constant. Atomic core level binding-energy shifts would thus arise (in the GPM approximation) through alteration of the sum in Equation (13). For example, to estimate the shift in binding energy of the ith core level in going from an atom A to a unipositive ion A^+ formed by loss of a valence electron from the kth orbital, one could simply delete from the sum the term corresponding to that valence orbital. Thus the difference

$$\Delta E_B^i = E_B^i(A^+) - E_B^i(A) \cong -\varepsilon_i(A^+) + \varepsilon_i(A)$$

$$\cong J_{ik} - \frac{1}{2} K_{ik} \quad ,$$

is a rather good estimate of the binding-energy shift[15]. In molecules the distribution of electronic charge is less clear-cut, and the estimation of shifts is a priori much more involved. The sum $\Sigma\ Z_n/r_n$ must be made over all the nuclei in each molecule. Also, the sum $\Sigma(2J_{ij} - K_{ij})$ may be taken over entirely different orbitals from one molecule to another. Thus there is no procedure analogous to omitting a single orbital as was done above for the atomic case. Instead shifts must be estimated by calculating differences in the electrostatic potential of a given core orbital from one molecule to another. Basch[16] and Schwartz[17] showed that shifts in the orbital energy of level i and in its potential energy are quite accurately related by

$$\Delta\varepsilon^i \cong \Delta V^i \quad . \tag{14}$$

Basch further showed that it isn't actually necessary to calculate the potential energy shifts of core electrons: shifts in the potential energy of an electron at the nucleus, ΔV_n, provide a very good approximation to ΔV^i, and

$$\Delta\varepsilon^i \cong \Delta V_n \quad . \tag{15}$$

The use of ΔV_n is equivalent to allowing the core orbital i to collapse to a point at the nucleus in calculating electrostatic repulsion integrals. The latter then become one-electron, rather than two-electron, integrals (and the exchange integrals are neglected), and the computation is greatly simplified. It is simplified further by the use of a theory such as CNDO[18], which assigns all of the electronic charge to specific atoms in a molecule. Siegbahn, et al.[11,19] used the host-atom charges q_i, plus the "external" molecular potential, V_i, as determined from CNDO calculations, to fit experimental shifts δE_B^i to the equation

$$\delta E_B^i = kq_i + V_i + \ell \quad , \tag{16}$$

where k and ℓ are least-squares fitted constants. Later, Davis, et al.[20,21], realized that fitting was not necessary: the CNDO model can be used directly to estimate shifts that are in quite good agreement with experiment, as described below.

Since CNDO theory already has several severe approximations, the way in which V_i is calculated using this theory is somewhat arbitrary. The problem is to construct an approach that is consistent with the CNDO philosophy--neglect of differential overlap--while still being tractable and physically reasonable. Other workers have simply set

$$V_i = \sum_j q_j e^2/R_{ij} \quad , \tag{17}$$

where eq_j is the net charge on atom j. This "point-charge" approach has much to recommend it. It is very easy to use, intuitively appealing, and a good approximation. There is, however, a straightforward way to improve on the point-charge model: namely, the direct calculation of r^{-1} matrix elements. This leads, as discussed below, to the "pp'" model for calculating V_i.

In CNDO theory molecular orbitals ψ_i are written as linear combinations of Slater atomic orbitals ϕ_j

$$\psi_i = \sum_j C_{ij}\, \phi_j \quad . \tag{18}$$

The zero differential overlap approximation

$$\langle \phi_j | \phi_k \rangle = \delta_{jk} \quad , \tag{19}$$

leads to the normalization condition

$$\sum_j C_{ij}^2 = 1 \quad , \tag{20}$$

for the (real) coefficients C_{ij}. Now since the error introduced by Equation (19)--Slater orbitals on different centers do not in fact have zero overlap--is not automatically propagated through new applications of the theory, it becomes necessary to make compensating approximations in applying CNDO wavefunctions in new ways. Let us write out a general expression for the contribution of the <u>electrons</u> in a molecule to the potential at the nucleus of atom a,

$$V_a^e = \langle \Psi | \sum_i^n \frac{e^2}{r_{ia}} | \Psi \rangle \quad . \tag{21}$$

Here i refers to the coordinates of the ith electron in the n-electron molecule, and Ψ is the antisymmetrized product of the <u>molecular orbitals</u> $\{\psi_j\}$. Because $1/r_{ia}$ is a one-electron operator and the molecular orbitals are orthogonal (they are eigenfunctions of the Fock operator, which is Hermitian[18]), one gets for V_a^e

$$V_a^e = \sum_i^n \int \psi_i(i) \frac{e^2}{r_{ia}} \psi_i(i) \, d\tau_i \quad .$$

When the molecular orbitals $\{\psi_i\}$ are expanded in terms of the atomic orbitals $\{\phi_j\}$, V_a^e becomes

$$V_a^e = \sum_i^n \sum_j \sum_k C_{ij}\ C_{ik} \int \phi_j(i)\ (e^2/r_{ia})\ \phi_k(i)\ d\tau_i$$

V_a^e can be reduced to three terms of the form

$$V_a^e = V_a^a \sum_{i,j} (C_{ij}^a)^2 + \sum_{i,j} (C_{ij}^b)^2 \langle \phi_j^b(i) | \frac{e^2}{r_{ia}} | \phi_j^b(i) \rangle$$

$$+ \sum_{i,j \neq k,k} (C_{ij}^b\ C_{ik}^c) \langle \phi_j^b(i) | \frac{e^2}{r_{ia}} | \phi_k^c(i) \rangle \quad . \tag{22}$$

In this notation the indices j and k refer to atomic orbitals. The index i refers, for brevity, both to the individual occupied molecular orbitals and to the coordinates of electrons in those orbitals. The superscript b refers to atoms other than a, while c refers to any atom. The first term in Equation (22) is easily identified: clearly

$$\sum_{ij} (C_{ij}^{a})^2 = Z_a' - q_a \quad , \tag{23}$$

where eZ_a' is the core charge of atom a, given by the nuclear charge minus the number of core electrons that are not considered in CNDO theory, and eq_a is the net charge on a (see Equation (16)). V_a^a in Equation (22) is just $e^2 \langle 1/r_a \rangle$ evaluated for electrons in atomic orbitals centered on atom a.

The second term in Equation (22) involves two-center integrals, but only one atomic orbital in each integral. To a good approximation

$$\langle \phi_j^b(i) | \frac{e^2}{r_{ia}} | \phi_j^b(i) \rangle \cong \frac{e^2}{R_{ab}} \quad . \tag{24}$$

In fact this relation is exact if $\phi_j^b(i)$ is an s orbital. It also holds under one of the usual assumptions of CNDO theory: that "other-center" integrals are independent of symmetry type. In this approximation, to which we shall return below, we would have the point-charge version of the CNDO potential model. This second term in Equation (22) is related to the V_i term in Equation (16).

The third term in Equation (22) involves two- and three-center integrals, with the atomic orbitals always on different centers. In the point-charge version of the CNDO-GPM approach, <u>these integrals are all neglected</u>,

and in the pp' version all but a certain subset are neglected. This is a very dubious approximation, because the integrals in this third term are not all small: for adjacent centers, the two-center integrals in the third term are comparable to the largest integrals in the second term. In rationalizing the neglect of the third term one might argue that this approximation is required for consistency since the integrals in this term involve differential overlap. Let us study this statement more closely, by means of a simple example.

Consider a diatomic molecule AB with an unpolarized bonding molecular orbital $|\psi\rangle$ which is a linear combination of atomic orbitals centered on A and B

$$|\psi\rangle = C|A\rangle + C|B\rangle \quad .$$

In a rigorous theory the potential at nucleus A arising from an electron in $|\psi\rangle$ would be given by

$$V_{RIG} = \frac{e^2}{2(1+S)} \left[\langle A(i)|\frac{1}{r_{iA}}|A(i)\rangle + \frac{1}{R_{AB}} + 2\langle A(i)|\frac{1}{r_{iA}}|B(i)\rangle \right] \quad , \tag{25}$$

where $S = \langle A|B\rangle$ is the overlap integral and we have assumed spherical symmetry for $|B\rangle$ to obtain the second term in brackets. In fact the three terms in brackets are related respectively to the three terms in Equation (22). In the CNDO approximation we would set $S = 0$ and (according to the approximation now under discussion) $\langle A(i)|(1/r_{iA})|B(i)\rangle = 0$, obtaining

$$V_{CNDO} = \frac{e^2}{2} \left[\langle A(i)|\frac{1}{r_{iA}}|A(i)\rangle + \frac{1}{R_{AB}} \right] \quad . \tag{26}$$

On comparing these two potentials, we find that the CNDO approximations incur an error of

$$V_{CNDO} - V_{RIG} = \frac{e^2}{(1 + S)} \left[\frac{S}{2} \left(\langle A(i) | \frac{1}{r_{iA}} | A(i) \rangle + \frac{1}{R_{AB}} \right) - \langle A(i) | \frac{1}{r_{iA}} | B(i) \rangle \right] . \tag{27}$$

One would expect this error to be small because the last term in square brackets should tend to cancel with the other terms. The cancellation would be exact if the off-diagonal element of 1/r were <u>exactly</u> the arithmetic mean of the two diagonal elements, times the overlap integral. This sounds intuitively like a reasonably good approximation: in fact it turns out to be more accurate than one might expect. To evaluate $V_{CNDO} - V_{RIG}$ in an important set of cases, we have evaluated the 1/r integrals for the electrostatic potential energy at a carbon nucleus, arising from an electron in an unpolarized C - X bond, with X = C, N, O, and F, and $R_{C-X} = 1.48$ Å, using the standard CNDO/2 wavefunctions in a $2p_\sigma - 2p_\sigma$ orientation. The results appear in Table 4. The difference $V_{CNDO} - V_{RIG}$ in Column 5 is encouragingly small ($\leqslant 0.6$ eV), thereby supporting in a quantitative way the approximation of dropping the third term in Equation (22). We should also note from this example, however, that $V_{CNDO} - V_{RIG}$ is not zero, and that the above estimate was based on the potential arising from a single electron. Thus we might expect, and indeed detailed comparisons with experiment have shown, that the CNDO potential approximation will have good predictive value for binding-energy shifts among similar molecules, because there can be considerable cancellation of $V_{CNDO} - V_{RIG}$ terms. By the same token, we must not expect such good agreement when <u>unlike</u> molecules are compared, especially if the number of

TABLE 4

ESTIMATE OF THE ERROR INCURRED, IN THE POTENTIAL ENERGY OF AN ELECTRON AT THE C NUCLEUS DUE TO AN ELECTRON IN THE C-X $2p_\sigma$ - $2p_\sigma$ BOND, BY THE CNDO APPROXIMATION. R = 1.48 Å. ENERGIES ARE IN a.u. EXCEPT AS NOTED.

X	S = $\langle 2p_\sigma(C) \| 2p_\sigma(X) \rangle$	A = $\frac{e^2}{1+S} \langle 2p_\sigma(C) \| \frac{1}{r_C} \| 2p_\sigma(X) \rangle$	B = $\frac{1}{1+S}\left[\frac{S}{2} \langle 2p_\sigma(C) \| \frac{e^2}{r_X} \| 2p_\sigma(C) \rangle + \frac{e^2}{R_{CX}}\right]$	$V_{CNDO} - V_{RIG}$ = B - A
C	0.332	0.167	0.145	-0.022(-0.59 eV)
N	0.319	0.148	0.141	-0.007(-0.20 eV)
O	0.291	0.128	0.132	0.004(0.10 eV)
F	0.257	0.108	0.119	0.011(0.30 eV)

bonds to the central atom can vary. This is a general observation about the CNDO potential model and it applies to both the GPM and the RPM modifications.

Returning now to the second term in Equation (22), the usual point-charge approximation to these two-center, one-orbital integrals (i.e., Equation (24)) is unnecessarily crude. With very little additional computing investment it is possible to evaluate the 1/r integrals directly. This allows a much more realistic evaluation of the contribution to the core-level potential at the central atom that arises from occupied p orbitals on neighboring atoms, a matter of some chemical importance. In the strict CNDO model (the point-charge model) an occupied atomic orbital on a neighboring atom would contribute a term e^2/R to the potential of the central atom whether the orbital in question had s or p character and (in the case of p character) regardless of its orientation. This result is exact for s orbitals or for filled shells, if exchange is neglected. It is, however, not very accurate for directed p orbitals. The region of the p orbital nearer the central atom will contribute most heavily to the 1/r integrals, and p_σ orbitals will therefore contribute more heavily than p_π orbitals to the potential. Thus, for example, for two carbon atoms at an internuclear distance R_{AB} = 1.50 Å, the n = 2 orbitals on atom B contribute to the potential energies at atom A in the amounts

$$V_A(2p_{\sigma B}) = \langle 2p_{\sigma B}(i)|1/r_{iA}|2p_{\sigma B}(i) = 10.77 \text{ eV}$$

$$V_A(2s_B) = \langle 2s_B(i)|1/r_{iA}|2s_B(i)\rangle = \frac{e^2}{R_{AB}} = 9.60 \text{ eV}$$

$$V_A(2p_{\pi B}) = \langle 2p_{\pi B}(i)|1/r_{iA}|2p_{\pi B}(i)\rangle = 9.01 \text{ eV} \quad .$$

These values were calculated using CNDO wavefunctions. We note that $[V_A(2p_{\sigma B}) + 2V_A(2p_{\pi B})]/3 = e^2/R_{AB}$, as expected in view of Unsold's Theorem. It is interesting to note the possibility of an atom B being slightly positively charged and yet exerting a repulsive potential on a core electron on atom A. This could happen if the electron population in the p orbitals of atom B were concentrated on p_σ orbitals. To avoid situations of this type and to establish some sensitivity to σ versus π bonding, we have therefore modified the CNDO potential model to include calculated 1/r integrals rather than just using point-charge estimates.

When 1/r integrals are computed a certain subset of the integrals in the third term of Equation (22) must be retained if the calculated potentials are to be invariant to coordinate transformations. These integrals are of the form $\langle p_B | 1/r_A | p_B' \rangle$, where p_B and p_B' are two different p orbitals on atom B. We have briefly alluded to this "pp' approximation" elsewhere, but have not explained it in detail before. It can be understood easily by referring to Figure 1. Let us calculate the potential at atom A arising from an electron in an orbital p_B centered on atom B and directed toward A in a p_σ orientation. If the coordinate axes are chosen to correspond to σ and π orientations as in Figure 1(a), only the diagonal elements $\langle p_x | r_A^{-1} | p_x \rangle$ and $\langle p_y | r_A^{-1} | p_y \rangle$ need be considered. In this example $p_B = p_x$ anyway: however, even if p_B were a linear combination of p_x and p_y the off-diagonal elements $\langle p_x | r_A^{-1} | p_y \rangle$ would vanish by symmetry.

Now suppose the axes were canted as in Figure 1(b): this will nearly always happen for some bonds in real molecules of any size. In this case the occupied σ orbital may be written as

$$p_B = C_x\, p_x + C_y\, p_y \quad ,$$

and

$$\langle r_A^{-1} \rangle = C_x^2 \langle p_x | r_A^{-1} | p_x \rangle + C_y^2 \langle p_y | r_A^{-1} | p_y \rangle + 2C_x C_y \langle p_x | r_A^{-1} | p_y \rangle \quad . \quad (28)$$

The last term clearly does not vanish by symmetry (although it is very small), and it must be retained to preserve invariance to coordinate transformations. Although integrals of this form are technically a subset of the third term in Equation (22), their retention is consistent with our other approximations if the r^{-1} integrals are calculated rather than estimated as point charges. In fact the calculation of the r^{-1} integrals leads to an inequivalence of $\langle p_{\sigma B} | r_A^{-1} | p_{\sigma B} \rangle$ and $\langle p_{\pi B} | r_A^{-1} | p_{\pi B} \rangle$ which then requires that $\langle p_x | r_A^{-1} | p_y \rangle$ be retained. Since $\langle p_B | r_A^{-1} | p_B \rangle$ is an absolute maximum in the σ orientation and an absolute minimum in the π orientation, it is obvious that $\langle r_A^{-1} \rangle$ would be too small if the third term were omitted in Equation (28) (note that $C_x^2 + C_y^2 = 1$). In going from Equation (28) to the point-charge approximation, however, the first two integrals must be replaced by $1/R_{AB}$ and the third by zero.

This completes our derivation of the ground-state potential model (GPM) for core-level binding-energy shifts, using CNDO molecular orbitals. The next section contains a summary of the approximations that are involved in the GPM, together with some calculated results. GPM results have been compared with experiment elsewhere[20-23]. We will not repeat these comparisons here, but will simply summarize the results by noting: (1) the pp' modification of the GPM usually shows agreement with experiment superior to that of the point-charge version; (2) the GPM shifts in C, N, O, and F usually show agreement with experiment to within a few tenths of an electron volt provided that comparisons are

restricted to similarly-bonded compounds. Figure 2 shows as an example a comparison of GPM predictions with experiment for C(1s) and F(1s) shifts in fluorinated methanes.

THE RELAXATION POTENTIAL MODEL (RPM)

In the second section the effect of relaxation on atomic binding energies was discussed, but the GPM approach calculates binding-energy shifts without regard to relaxation. It is straightforward to include relaxation in molecules by using an "equivalent-cores" approximation similar to that described for atoms in that section. In CNDO theory this approximation is introduced very simply, by replacing the active atom with an atom of the next element (thus N for C, F for O, etc.) and repeating the calculation using the same molecular geometry but one fewer electron. This approximation can be derived from a result discovered by Liberman[24] and derived by Hedin and Johansson[6]. In terms of the 1s binding energy this result is

$$E_B(1s) = -\frac{1}{2}\left[\varepsilon(1s) + \varepsilon(1s)^*\right] \quad , \tag{29}$$

where $\varepsilon(1s)$ and $\varepsilon(1s)^*$ are respectively the 1s orbital energies in the ground state and the 1s hole state. Writing this relation in the form of binding energy <u>shifts</u> between two molecules, we can make the following series of approximations:

$$\Delta E_B = -\frac{1}{2}\left[\Delta\varepsilon(1s) + \Delta\varepsilon(1s)^*\right] \tag{30a}$$

$$\Delta E_B \cong -\frac{1}{2}\left[\Delta V(1s) + \Delta V(1s)^*\right] \tag{30b}$$

$$\Delta E_B \cong -\frac{1}{2}\left[\Delta V_n + \Delta V_n^*\right] \tag{30c}$$

$$\Delta E_B \cong -\frac{1}{2}\left[\Delta V_n + \Delta V_n(Z+1)\right] \quad . \tag{30d}$$

Here Equation (30b) refers to the approximation of replacing 1s orbital-energy shifts by shifts in the potential energies of the 1s orbitals. Equation (30c) is the further approximation of using shifts in the potential at the nucleus, and Equation (30d) is the equivalent-cores approximation. Combining the relaxation correction with the potential model for binding-energy shifts, we therefore arrive at expression Equation (30d) for the Relaxation Potential Model (RPM), to be compared with the GPM expression

$$\Delta E_B = -\Delta V_n \quad . \tag{31}$$

It is instructive to rewrite Equation (30d)

$$\Delta E_B = -\Delta V_n - \Delta V_R \quad , \tag{32}$$

where

$$V_R = \frac{1}{2}\,[V_n(Z + 1) - V_n] \quad , \tag{33}$$

is the <u>relaxation energy</u> in the RPM approximation. Table 5 lists values of V_R(C 1s) for the fluorinated methanes, and compares them with estimates from <u>ab initio</u> hole-state calculations. The good agreement of V_R with <u>ab initio</u> results (which are themselves apparently quite sensitive to the basis set chosen) is very encouraging: Of special note is agreement in the <u>trend</u> in V_R from CH_4 to CF_4--a decrease of $\sim$ 1 eV--which alone is important in estimates of binding-energy shifts. We shall discuss these two topics in turn.

The relaxation energies V_R estimated above are expected to be fairly accurate for essentially the same reasons that applied to the analogous atomic

TABLE 5

CARBON 1s RELAXATION ENERGIES IN THE FLUOROMETHANES (eV)

Molecule	Ab Initio I[a,c]	Ab Initio II[b,c]	V_R[d]	V_R'[e]
CH_4	14.31	12.1	15.89	14.4
CH_3F	13.78	11.6	15.92	14.4
CH_2F_2	13.69	11.8	15.73	14.2
CHF_3	13.58	11.7	15.38	13.9
CF_4	13.53	--	14.91	13.5

[a]From E. Clementi and A. Routh, Int. J. Quantum Chem. 6, 525 (1972).

[b]From C. R. Brundle, M. B. Robin, and H. Basch, J. Chem. Phys. 53, 2196 (1970).

[c]Ref. a employed a slightly larger basis set than ref. b; the relaxation energies were determined by subtracting the calculated binding energy ($E_{ion} - E_{ground\ state}$) from the calculated orbital energy.

[d]From Equation (33).

[e]$V_R' = 0.905\ V_R$. See Table 6 and related discussion.

relaxation energies estimates in Table 1. In fact these molecular estimates might be expected to be somewhat better because the error incurred by substituting $\Delta \langle 1/r \rangle$ values for changes in combinations of Coulomb and exchange integrals is maximal for valence electrons on the central atom. Thus since exchange between the central atom's 1s electrons and electrons in orbitals on other atoms is negligible anyway, its neglect in the above $\Delta \langle 1/r \rangle$ approximation to V_R is of no consequence. It should be emphasized that while the objections to the approximations made in the GPM approach (see the discussion following Equation (22)) are equally valid for the $V_n(Z + 1)$ term in the RPM approximation, these objections apply with much less force to the RPM estimation of the difference V_R in Equation (33). The reason for this is that the V_R estimate is closely related to electrostatics in that it measures the response of a charge distribution to the sudden appearance of a positive charge. Errors in the charge distribution are of less consequence in estimates of V_R, for which the molecular geometry is fixed, than in predicting ΔV from one molecule to another.

From the above argument we may infer that it is worthwhile to evaluate the error incurred in the RPM estimate of V_R by the $\Delta \langle 1/r \rangle$ approximation. To this end we have compared in Table 6 the values of $V_R(1s)$ as calculated in the equivalent-cores approximation for atomic $C(2s^2 2p^2)$, $N(2s^2 2p^3)$, $O(2s^2 2p^4)$, and $F(2s^2 2p^5)$, using Mann's[8,13] atomic integrals. This comparison shows the RPM estimates to be 8 - 10% high. Applying the ratio

$$\frac{V_R(\Delta F, G)}{V_R(\langle 1/r \rangle)} = 0.905$$

TABLE 6

ATOMIC 1s-ORBITAL RELAXATION ENERGIES FROM EQUIVALENT-CORES ESTIMATES (IN eV), USING MANN'S INTEGRALS (REFS. 8, 13)

Method	$C(2s^2 2p^2)$	$N(2s^2 2p^3)$	$O(2s^2 2p^4)$	$F(2s^2 2p^5)$
$\Delta \langle r^{-1} \rangle$	19.0	23.5	27.8	32.2
ΔF^0 [a]	17.7_5	22.0	26.3	30.6
$\Delta(F,G)$ [b]	17.2	21.4	25.6	29.8
$\Delta(F,G)/\Delta \langle r^{-1} \rangle$	0.905	0.911	0.921	0.925

[a] Using 1s - 2s,p Coulomb integrals only.

[b] Using Coulomb and exchange integrals.

for atomic carbon in Table 6 to the RPM estimates of V_R in Table 5 (an admittedly rather crude correction), we obtain the values of $V_R' = 0.905$ shown in the last column of Table 5. They agree quite well with the ab initio values, thereby increasing our confidence in the RPM approach for estimating V_R.

One possible application of V_R (or V_R') values obtained from the RPM model would be in calculating binding energies in molecules for which ab initio orbital energies in the ground state were available. For a molecule containing N inequivalent atoms, this approach would yield all N core-level binding energies without the N additional ab initio hole-state calculations that would otherwise be required. The binding energies would be given by

$$E_B(i) = -\varepsilon(i) - V_R'(i) \quad , \tag{34}$$

where i refers to any of the inequivalent core-level holes.

We turn now to trends in V_R. These can be best understood if we establish an intuitive picture of the dynamic relaxation process that accompanies photoemission. In atoms this relaxation occurs adiabatically, as discussed in the second section. The relaxation energy is a consequence of the increase in the repulsive contribution to the potential of the core level by electrons in outer orbitals, due to their relaxing toward the core-level hole. The same effect occurs in molecules, but with a larger relaxation energy because additional electrons can relax toward the hole through bonds. In fact calculated values of V_R, which are set out for a number of molecules in Table 7, show a marked tendency to increase with molecular size. A nice intuitive way to think of this relaxation phenomenon is to consider the fate of the unbalanced "positive" hole-state charge that is created on

TABLE 7

CALCULATED POTENTIALS (IN eV) AND CHARGES (IN UNITS OF |e|)

Molecule	V(Z)	V(Z + 1)	V_R	q(Z)	q(Z + 1)
		Carbon Nuclei			
CO	88.21	112.03	11.92	+0.04	+0.58
CO_2	82.31	108.02	12.86	+0.54	+0.76
HCN	88.57	117.36	14.40	+0.03	+0.21
CF_4	77.75	107.56	14.91	+0.81	+0.73
HCOOH	84.37	114.98	15.31	+0.38	+0.37
CF_3H	80.34	111.10	15.38	+0.61	+0.51
C_2H_4	88.89	119.74	15.43	-0.06	-0.01
C_2H_2	89.27	120.42	15.58	-0.06	-0.08
CF_2H_2	83.06	114.52	15.73	+0.40	+0.30
$CH_3 - C^*F_3$	80.84	112.56	15.86	+0.60	+0.54
CH_4	88.88	120.65	15.89	-0.05	-0.09
CFH_3	85.89	117.73	15.92	+0.18	+0.10
$C^*F_3CH_2NH_2$	80.89	112.88	16.00	+0.60	+0.54
$H_3C - C^*F_2H$	83.22	115.44	16.11	+0,42	+0.36
CH_3OH	87.01	119.27	16.13	+0.14	+0.07
$CF_3 - CF_3$	79.18	111.56	16.19	+0.56	+0.48
$H_2C = C^*F_2$	83.02	115.51	16.25	+0.44	+0.40
$H_3C - C^*FH_2$	85.82	118.42	16.30	-0.05	-0.06
$C^*F_3 - CF_2 - CF_3$	79.11	111.94	16.42	+0.58	+0.50
$CH_3 - CH_3$	88.54	121.56	16.50	0.00	-0.03
$CH_2 = C^*HF$	85.93	118.97	16.52	+0.21	+0.18
$C^*H_3 - CH_2F$	88.10	121.15	16.53	+0.21	+0.16

(continued)

TABLE 7 (continued)

Molecule	V(Z)	V(Z + 1)	V_R	q(Z)	q(Z + 1)
		Carbon Nuclei			
$H_2C\overset{O}{\frown}CH_2$	86.95	120.01	16.53	+0.09	+0.06
$CHF = C^*F_2$	82.57	115.73	16.58	+0.39	+0.34
$C^*H_3CH_2NH_2$	88.69	121.94	16.65	-0.03	-0.05
$C^*H_3 - CHF_2$	87.70	121.12	16.71	-0.08	-0.10
$C^*H_3 - CF_3$	87.18	120.68	16.75	-0.11	-0.11
$C^*H_2 = CHF$	88.66	122.42	16.88	-0.11	-0.10
$(C^*H_3)_2CHNO_2$	87.50	121.35	16.93	-0.02	-0.05
$C^*HF = CF_2$	85.28	119.20	16.96	+0.07	+0.05
$C^*H_2 = CF_2$	88.30	122.28	16.99	-0.18	-0.16
CH_3NO_2	85.87	119.86	16.99	-0.03	-0.09
$CF_3 - C^*F_2 - CF_3$	80.93	115.52	17.30	+0.28	+0.22
1,3,5-$C_6H_3F_3$ (C_F carbon)	84.50	119.36	17.43	+0.28	+0.26
$(CH_3)_2C^*HNO_2$	85.79	120.92	17.57	+0.05	+0.03
cyclo C_4F_6 (CF_2 carbon)	80.85	116.10	17.63	+0.37	+0.29
cyclo C_4F_8	81.16	116.45	17.65	+0.33	+0.24
para $C_6H_4F_2$ (C_F carbon)	85.40	120.70	17.65	+0.22	+0.19
C_6H_6	88.31	123.68	17.69	+0.01	+0.01
para $C_6H_4F_2$ (C_H carbon)	87.63	123.23	17.80	-0.03	-0.03
1,3,5-$C_6F_3H_3$ (C_H carbon)	87.91	123.79	17.94	-0.14	-0.12
C_6F_6	83.68	119.58	17.95	+0.16	+0.13
cyclo C_4F_6 (C_F carbon)	84.03	119.96	17.97	+0.13	+0.08

(continued)

TABLE 7 (continued)

Molecule	V(Z)	V(Z + 1)	V_R	q(Z)	q(Z + 1)
		Nitrogen Nuclei			
NO	132.43	163.89	15.73	+0.04[a]	+0.50[a]
N_2	133.22	166.56	16.67	0.00	+0.38
NN^*O	124.82	161.26	18.22	+0.47	+0.56
HCN	134.47	171.46	18.50	-0.10	+0.21
NH_3	135.54	173.56	19.01	-0.23	-0.10
N^*NO	132.52	170.99	19.24	-0.15	+0.15
NF_3	125.34	163.98	19.32	+0.36	+0.44
CH_3NH_2	135.17	174.67	19.75	-0.19	-0.05
$H_2N - NH_2$	134.46	174.41	19.98	-0.13	-0.03
NF_2	131.24	171.35	20.00	+0.23[a]	+0.53[a]
CH_3NO_2	124.22	164.22	20.00	+0.50	+0.48
NO_2	125.58	166.36	20.39	+0.48[a]	+0.63[a]
$(CH_3)_2CHNO_2$	124.67	165.61	20.47	+0.47	+0.46
$C_6H_5NO_2$	125.04	166.26	20.61	+0.47	+0.47
NOF_3	119.46	160.71	20.63	+0.70	+0.58
N_2F_4	127.76	173.73	22.99	+0.16	+0.07
		Oxygen Nuclei			
O_2	185.30	214.06	14.38	0.00[a]	+0.30[a]
NO	185.94	226.63	20.35	-0.04[a]	+0.30[a]
NO_2	188.29	228.98	20.35	-0.24[a]	+0.12[a]
H_2O	192.22	233.47	20.63	-0.41	-0.04
NNO	191.02	233.80	21.39	-0.32	+0.15
CO	187.39	230.31	21.46	-0.04	+0.25

(continued)

TABLE 7 (continued)

Molecule	V(Z)	V(Z + 1)	V_R	q(Z)	q(Z + 1)
		Oxygen Nuclei			
CH_3OH	189.97	234.32	22.18	-0.26	-0.47
HCO^*OH	191.38	237.97	22.36	-0.30	0.00
CH_3CH_2OH	190.12	235.44	22.66	-0.26	+0.03
C_2H_4O	189.79	235.42	22.82	-0.21	+0.11
CH_3NO_2	191.33	237.60	23.14	-0.33	+0.03
$HCOO^*H$	188.16	232.88	23.30	-0.24	+0.07
$(CH_3)_2CHNO_2$	191.58	238.65	23.54	-0.33	+0.01
$C_6H_5NO_2$	191.88	239.45	23.79	-0.34	0.00
$(CH_3CH_2)_2O$	189.92	238.24	24.16	-0.23	+0.02
C_4H_4O (furan)	189.10	237.64	24.27	-0.19	+0.05

[a]The values were calculated by R. L. Martin for ref. 27 using INDO orbitals.

photoemission. The inward polarization of negative electronic charge to shield the core hole is approximately describable as outward expansion of a unit of positive charge due to self-repulsion. Thus we would expect the final state of a diatomic molecule to show an electron population distribution similar to the initial state, but with an additional charge of $\sim + e/2$ on each atom (this does not imply that the core hole is delocalized: it is not). Similarly in a symmetrical molecule such as CH_4 or CF_4 the C(1s) hole state should have $\sim + e/4$ additional charge on each ligand. This picture is only qualitative: it doesn't account for subtle chemical effects in a highly-polar molecule. Nevertheless it gives a perhaps surprisingly accurate prediction of charge distributions in final states. Table 7 lists, in addition to V_R, V_n, and $V_n(Z + 1)$, the RPM estimates of initial- and final-state central-atom charges in the molecules listed. From these charges we can deduce that the additional charges after 1s photoemission on the two atoms of N_2 and CO are $N^*(+0.38) - N(+0.62)$, $C^*(+0.54) - O(+0.46)$, and $C(+0.71) - O^*(+0.29)$, in rough agreement with the above estimates of +1/2 for each atom. In CH_4 and CF_4 the ligand atoms gain +0.26 and +0.27 units of charge, respectively, in excellent agreement with the predictions.

Entries in Table 7 are listed in order of increasing V_R. The predicted shifts have been compared with experiment elsewhere[20-23]. For brevity we shall simply note here that agreement is very good, especially for the RPM approximation. A few applications of the results in Table 7 are made in the next section. To indicate the importance of the relaxation energy term, we note the total range of 1s binding-energy shifts for these second-row elements is $\sim$ 12 eV or less, while V_R can vary by up to 10 eV (although exclusion of di- and triatomics reduces this range to 4 eV). <u>Relaxation therefore cannot</u>

be neglected in assessing binding-energy shifts. Even *ab initio* orbital energies should not correlate well with experimental binding energies if molecules with very different relaxation energies are compared.

We close this section by noting from Table 7 three additional trends in V_R for C(1s) holes, apart from the major trend of an increase of V_R with molecular size. These are a (related) increase in V_R as ligands are added to an atom, a slight decrease in V_R on substitution of F for H, and a tendency for unsaturated or cyclic systems to have large values of V_R.

APPLICATIONS AND SUMMARY

The principle object of this paper was to describe the calculation of core-level binding-energy shifts from potential models that were applicable to "intermediate-level" molecular wavefunctions. Comparisons with experiment are described in detail elsewhere[20-23]. In this section we simply indicate some of the applications of both GPM and RPM theory. Finally a brief summary is given of the approximations entailed in these two approaches.

Some Applications of the GPM Method

Detailed comparisons with experiment[20-23] have shown that GPM predictions based on CNDO/2 wavefunctions give core-level shifts in excellent agreement with experiment, provided that only similar molecules are compared. From the discussions in the last section and following Equation (22) we may infer that "similar" in this context would preclude comparison of large and small molecules, of molecules with different numbers of bonds to the central atom, of cyclic or unsaturated molecules with saturated, straight-chain molecules, and perhaps of fluorine-substituted with unsubstituted hydrocarbons. In fact

only the first three restrictions are quantitatively very important. Thus standard deviations of from 0.1 to 0.4 eV in comparisons between theoretical GPM C(1s) shifts and experiment were obtained for fluorinated alkanes[22], benzenes[21], ethanes[23], and ethylenes[23]. The advantages of comparing only molecules with the same number of bonds to the central atom have been noted for O(1s) shifts[23].

The atomic-charge (or ACHARGE) analysis[21], which has been reported in several very similar variants[21,25,26], is closely related to the GPM model in its point-charge version. The difference is that ACHARGE yields an experimental set of atomic charges $\{q_i\}$ from the measured binding-energy shifts $\{\delta_i\}$ through solution of the equation

$$\vec{\delta} = \underline{\underline{A}}\,\vec{q} \quad , \tag{35}$$

where the matrix elements A_{ij} depend only on molecular geometry and the <u>atomic</u> integral V_a^a in Equation (22) (or k in Equation (16)). ACHARGE atomic charges generally show very good to excellent agreement with CNDO charges. We have discussed this conclusion elsewhere[21,23] and will simply illustrate it here by plotting in Figure 3 the two sets of charges for H, C, and F as derived from[27] fluorinated hydrocarbons[21,23]. These values of q (ACHARGE) were all obtained from binding energies measured in gases. We believe that they are to be preferred over results from solids[25,26], for which lack of a suitable reference level precludes a rigorous determination of shifts. The good agreement in Figure 3 suggests that chemists may have in binding-energy shifts an operational means for determining that elusive quantity, the atomic charge.

The GPM method is also useful in calculating diamagnetic shielding corrections for NMR spectra. Basch showed[16] the connection between the average

diamagnetic shielding constant σ^d_{Av} and binding-energy shifts. This can be written[16]

$$\Delta\sigma^d_{Av} \text{ (in ppm)} = 0.65\left(\Delta V_a(Z) + e^2 \sum_j \frac{Z_j}{R_{aj}}\right) \text{ (in eV)} \quad , \tag{36}$$

after substitution of appropriate values for physical constants.

Since this pp' GPM calculation predicts binding energies to $\sim$ 1 eV, it follows that this equation gives diamagnetic shielding constants to $\sim$ 1 ppm or better in most cases.

Typical Applications of the RPM Method

The RPM method is likely to be of particular value in calculating shifts for cases in which variations in V_R can affect the observed shifts. Thus the N(1s) shifts in several small molecules are predicted much better by RPM than by GPM calculations, with standard deviations of 1.3 eV and 2.35 eV, respectively[22].

The C(1s) shift in carbon monoxide is very badly predicted by the GPM method because CO is compared with larger molecules. The predicted value for E_B(C 1s;CO) is relatively too low in GPM because CO has a much smaller value of V_R than the other molecules. The RPM approach brings CO into reasonable agreement[22].

There are also cases in which poor agreement between GPM predictions and experiment is obtained even though chemically similar compounds are being compared. Ammonia and the methylamines provide an example. The GPM theory

predicts E_B(N 1s) to increase by 1 eV from NH_3 to $(CH_3)_3N$, whereas it in fact decreases by 0.8 eV in excellent agreement with RPM predictions[23]. Similar behavior has been observed and explained in nitroxides[27].

A solid-state problem of some interest is the relative C(1s) binding energies in graphite and diamond. The most accurate experimental values of E_B(C 1s) for these two cases are[28,29]

$$E_B^F(\text{C 1s, diamond}) = 284.44(7)\ \text{eV}$$

$$E_B^F(\text{C 1s, graphite}) = 284.68(20)\ \text{eV} \quad .$$

Since the graphite work function is known to be 4.6 V[30], we also have its binding energy relative to the vacuum level,

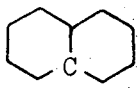
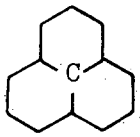
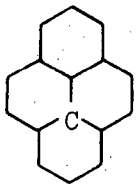
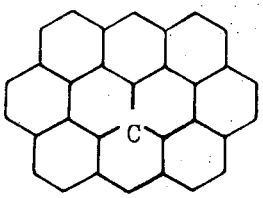
$$E_B^V(\text{C 1s, graphite}) = 289.3\ \text{eV} \quad .$$

CNDO calculations for these (infinite) lattices are of course not possible, but we have calculated C(1s) relaxation energies using the RPM method for a number of two-dimensional hexagonal arrays of carbon atoms, to simulate the graphite lattice. The outer carbons were taken as being bonded to avoid "dangling bonds" and open orbitals, so this calculation was in fact done on the most central carbon atoms in the planar aromatic molecules benzene, anthracene, etc., as shown in Table 8. There is a clear tendency for V_R(C(1s)) to increase with increasing molecular size. We plotted V_R against (n_C = number of carbons)$^{-1/2}$, and extrapolated to $n_C^{-1/2} = 0$ to obtain the limiting value

$$V_R(\text{graphite}) \cong V_R(C_6H_6) + (1.6 \pm 0.2)\ \text{eV} \quad .$$

TABLE 8

POTENTIAL AT CARBON ATOMS IN MOLECULES SIMULATING GRAPHITE ENVIRONMENT (IN eV)

Molecule[a]	n_C	V(Z)	V(Z + 1)	V_R
	6	88.31	123.68	17.69
	10	87.79	123.93	18.07
	13	88.03	125.36	18.66
	16	87.77	125.03	18.63
	32	87.91	126.18	19.14

[a]Potential is calculated at carbon indicated by "C".

The $n_C^{-1/2}$ plot was chosen in the expectation that the excess positive charge in the relaxed final state would go to a radius $R \propto n_C^{1/2}$ on the outside of the molecule, when it would exert a potential $V \sim e^2/R \sim e^2/n_C^{1/2}$ on the hole state. A $1/n_C$ extrapolation would yield essentially the same result. Since the measured C(1s) binding energy in benzene is 290.4 eV[21], an additional relaxation energy of 1.6 eV would give E_B(graphite, theory) = 288.8 eV. An alternative estimate of 289.3 eV was obtained by extrapolating the RPM estimates of E_B, and comparing with the benzene value. Thus we estimate a "best value" of

$$E_B(\text{graphite, theory}) = 289.0 \pm 0.3 \text{ eV} \quad ,$$

in good agreement with the experimental value of 289.3 eV. Thus it is possible to make an estimate of a core-level binding energy in a solid from RPM theory. A similar estimate was made for diamond, based on only methane and neopentane. The result was

$$E_B(\text{diamond, theory}) = 288.2 \pm 0.5 \text{ eV} \quad .$$

This could be compared with experiment if the work function of diamond were known.

Summary of the GPM and RPM Approximations

The two models for calculating core-level binding-energy shifts from CNDO wavefunctions may be summarized as follows:

1. In both cases the core-level shifts are approximated by shifts in the potential at the nucleus: $\Delta E_B \cong -\Delta V_n$. Thus the spatial extent of the core state is neglected, as are shifts in exchange terms involving it.

2. In the point-charge modification of GPM or RPM, the potential due to other atoms is approximated by a term of the form $\Sigma q/R$. This version is most directly comparable with the ACHARGE model.

3. In the pp' modification of GPM or RPM, r^{-1} integrals are calculated. For invariance to coordinate transformations this necessitates retention of certain additional (pp') terms in the potential.

4. In the RPM approach, the effect of a core hole state on the potential is simulated by repeating the CNDO calculation with the nuclear charge on the central atom increased by one unit. Binding energy shifts are then given by $-(1/2)\Delta[V_n(Z) + V_n(Z + 1)]$, and the relaxation energy by $(1/2)[V_n(Z + 1) - V_n(Z)]$.

All these modifications are remarkably successful in predicting core-level binding-energy shifts. The pp' modification of RPM is the soundest theoretically and it also agrees best with experiment.

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FIGURE CAPTIONS

Figure 1. Illustration of the necessity for retaining the $\langle p|r^{-1}|p' \rangle$ matrix elements. In (a), the x coordinate axis is collinear with the A - B bond; thus $p_\sigma = p_x$ and only $\langle p_x|r^{-1}|p_x \rangle$ matrix elements need be considered in calculating the potential at A due to this orbital. In (b) the axes are tilted and $\langle p_x|r^{-1}|p_y \rangle$ are nonzero and must be retained.

Figure 2. Comparison of C(1s) shifts from various GPM calculations with experiment for the fluorinated methanes.

Figure 3. Atomic charges on C, F, and H in units of $|e|$ from CNDO/2 calculations, versus charges derived from ACHARGE analysis of binding energy shifts, for 27 fluorinated hydrocarbons. The range of charges found on the following types of atom are indicated: F, H, and carbon bonded to H (C_H); to fluorine (C_F) and to two, three, or four fluorines (C_{F2}, C_{F3}, C_{F4}).

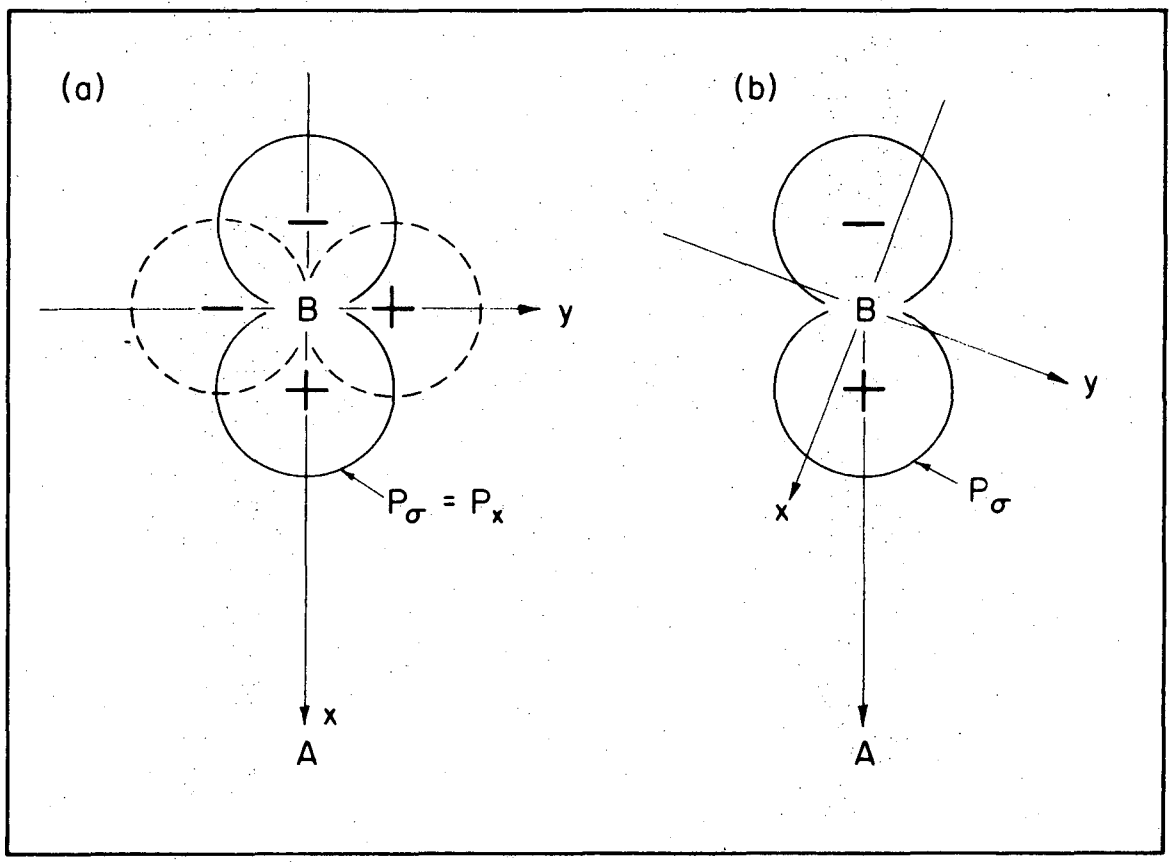

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Fig. 1

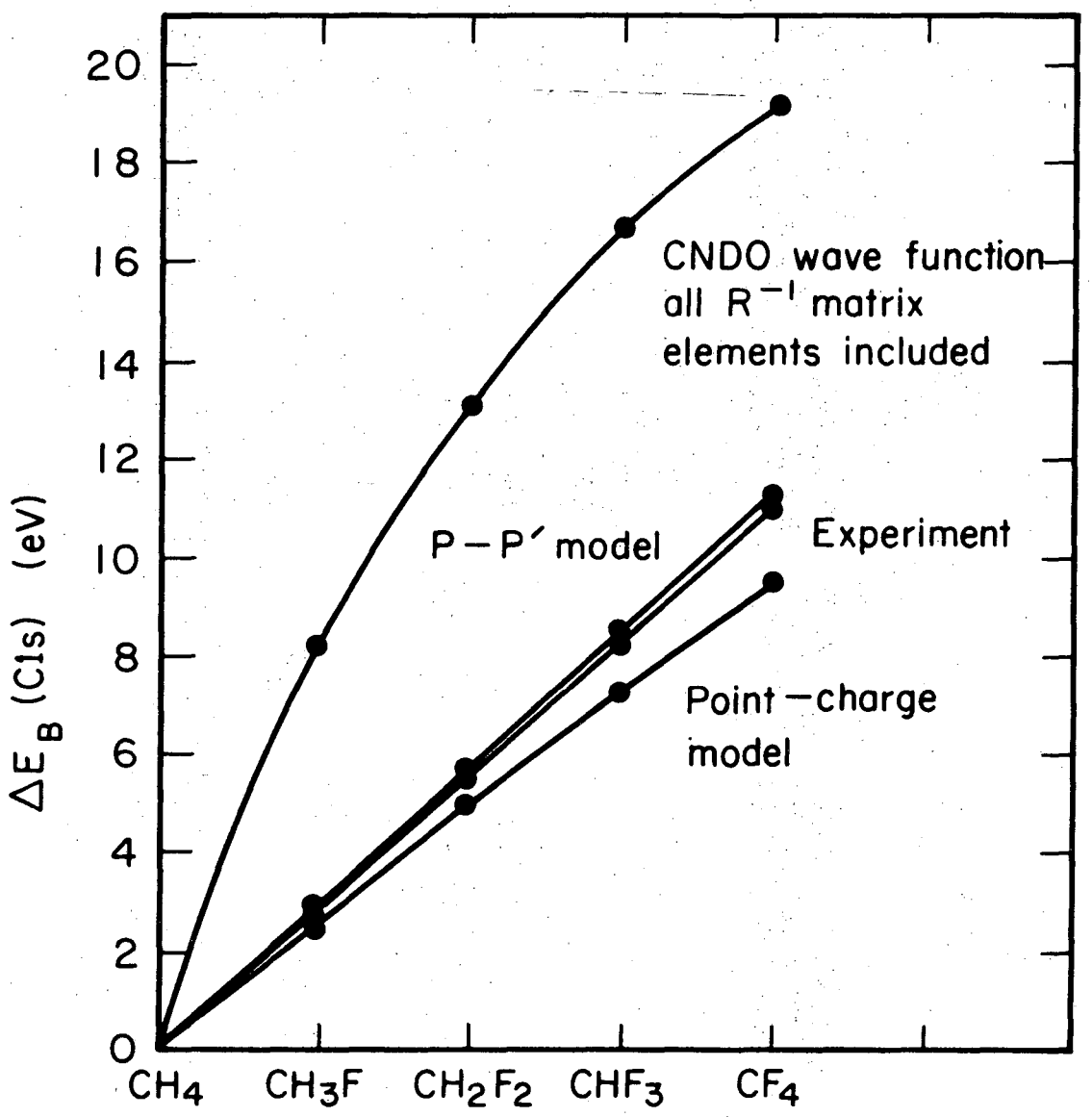

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Fig. 2

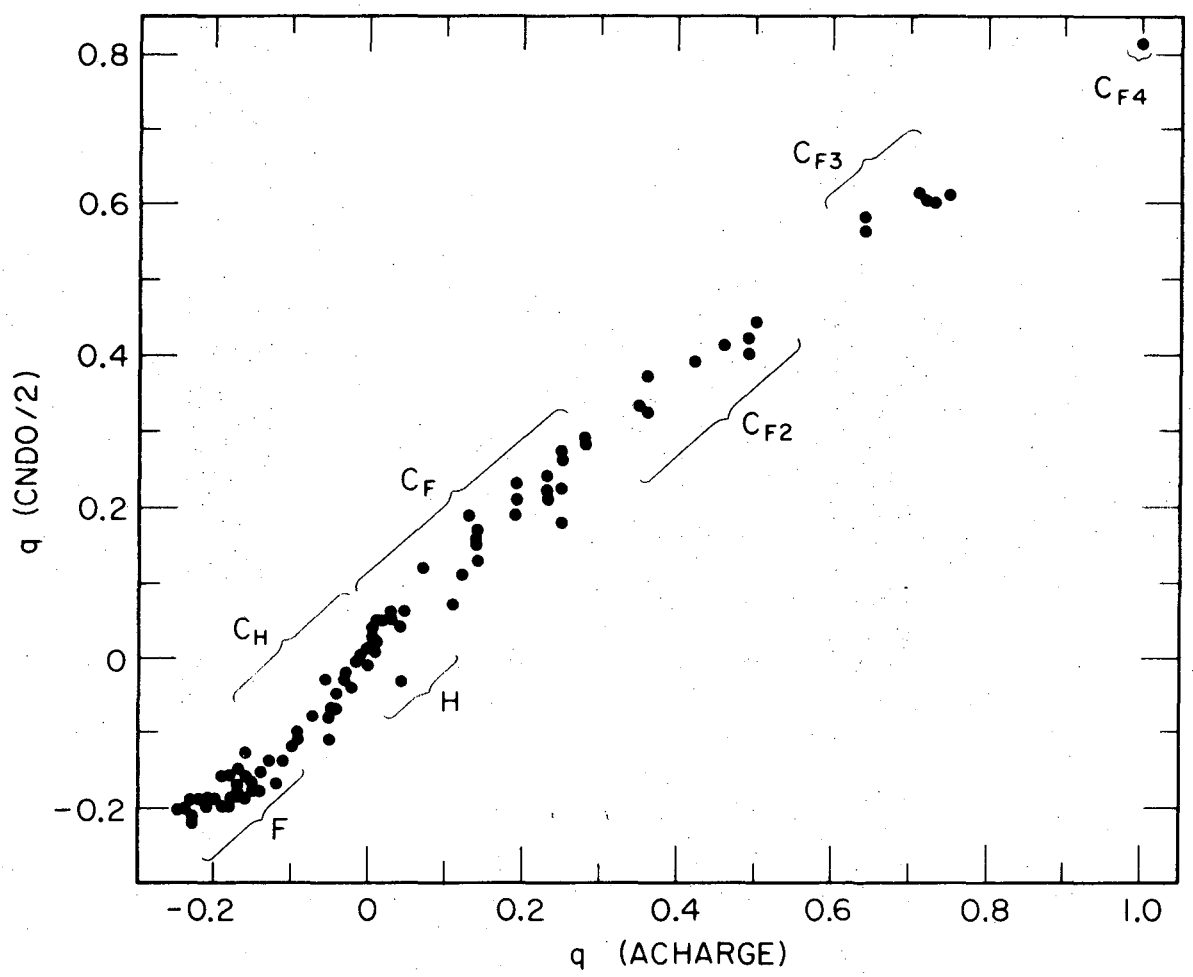

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Fig. 3

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