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Inner-Shell Eigenvalues from Valence Orbital only Calculations

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Methods are examined for calculating Inner-shell Eigenvalues from molecular orbital models which do not explicitly include core basis functions. If the "valence-orbital only" calculation is a good one, a rather straightforward method can be used to obtain core eigenvalues with a rms error of ±0.01 a.u. compared with *ab-initio* values. Even simpler methods can be used to reproduce trends among core eigenvalues. The AAMOM valence technique, and to a lesser extent, the INDO model, can be used to yield core eigenvalues for orbitals centered on carbon and nitrogen: for oxygen the agreement is poorer. Extended Hückel or Iterative Extended Hückel methods cannot be used for this purpose with any degree of confidence.

Eigenvalues from *ab-initio* studies or from AAMOM and INDO can be used in assigning ionization processes (XPS) from orbitals localized on carbon and nitrogen: ionization processes from oxygen orbitals are not well treated. An attempt is made to explain this behaviour.

Key words: Inner-shell eigenvalues – X-ray photoelectron spectra – ESCA

1. Introduction

The great majority of quantum mechanical calculations performed on the larger molecules of current experimental interest are of a semi-empirical or approximate nature. Such calculations have proven of great value in estimating features of the molecular orbital structure: orbital symmetries, gross charge distribution, spectra, molecular conformation, and even estimates of heats of formation, etc. Most of these calculations are of "valence-orbital only" type, incorporating the major influences of the core or inner shell through parametrization or through pseudo-potentials [1].

More recently, however, a great deal of interest has been focused specifically on the inner shell, as ionization processes from this shell have become accessible through the general technique of Electron Spectroscopy for Chemical Analysis, ESCA [2, 3]. Techniques such as X-ray Photoelectron Spectroscopy (XPS) and X-ray UV Spectroscopy (XUV) have demonstrated that core ionization processes can be measured with sufficient accuracy to distinguish atomic environment, to facilitate qualitative and quantitative chemical analysis, as well as showing strong promise in studying surface phenomena [2].

From the quantum mechanical standpoint two approaches have dominated in explaining these chemical shifts; i.e. the shift of ionization energy of the core electrons in molecules relative to standard values, or to one another:

1. Koopmans' approximation [4]: The inner shell molecular orbital eigenvalues are compared with the negative of the observed ionization energies.

2. ΔE(SCF): This method relies on the difference of energies calculated for the atom or molecule after and before the ionization process. Most often the calculations are of the Hartree-Fock Self Consistent Field (SCF) type, although they need not be. As a separate calculation is required for the neutral species and each ionized state (center), this method is considerably more difficult to implement than trusting Koopmans' Approximation.

We wish here to first focus our attention on the calculation of core eigenvalues, $\varepsilon_{\text{core}}$, from "valence orbital only" calculations. This is of interest for its own sake to complete the molecular orbital eigenvalue spectrum. We will then compare the calculated core eigenvalues with experimental ionization potentials. In developing methods for calculating inner shell eigenvalues we shall examine each step in the approximations used in deriving the popular "charge potential model" of Siegbahn and co-workers [2, 3] used to explain inner shell ionization. We assume for the moment that the eigenvalues of a "good" molecular orbital calculation reflect the ionization energies obtained experimentally. The question then arises of how the popular valence shell calculations (one which, by construction, does not include the core explicitly) can be made to successfully yield core eigenvalues.

We take the following approach: Given an accurate "valence-orbital only" calculation, what is the minimum amount of work required to accurately reproduce inner shell eigenvalues? For this purpose we examine model *ab-initio* calculations

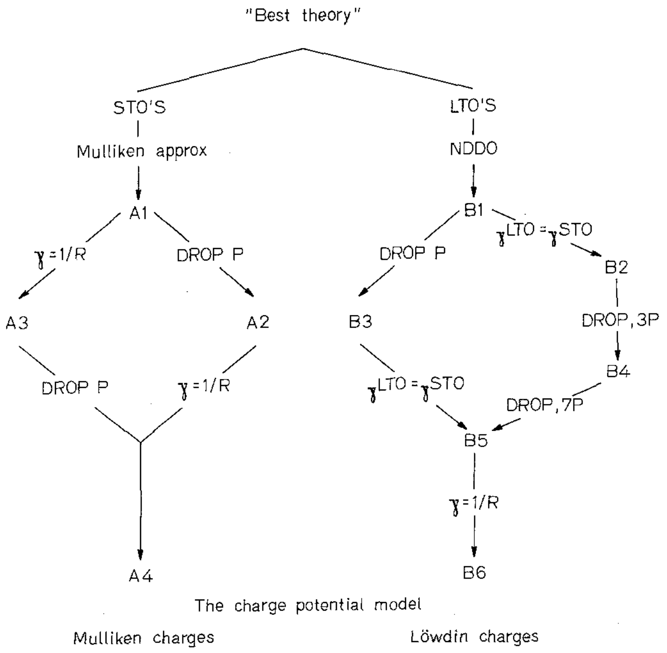

Fig. 1. Approximations consistent with current semi-empirical molecular orbital theories

and attempt to match the core eigenvalues of these calculations from properties of the valence shell only. The simplest theory that accomplished this compromise between ease and accuracy we call our "best theory". Any valence shell only calculation which reflects accurately the *ab-initio* density should yield identical inner shell eigenvalues using this theory. Very often, however, the Fock-Dirac density calculated from approximate methods relates to basis sets that are unknown other than in their effect in the evaluation of integrals. For this reason we relax certain aspects of our "best theory" consistent with the integral approximations in the more popular methods. Thus we here examine two philosophies: the first one is that we do not care *where* or *how* the Fock-Dirac density is obtained, but once obtained it accurately reflects an *ab-initio* calculation with either a Slater Type Orbital (STO) basis [5] or a symmetrically orthogonalized Löwdin Type Orbital (LTO) basis [6]. Since the transformation between these two bases is known we insist that the consistent application of our "best theory" yield identical results for the same calculation in either basis. This places restrictions on the derivation of this formulation. The second philosophy examined assumes that the basis of the approximate calculation is neither STO nor LTO, but is defined by the details of the molecular orbital calculation itself. We then make approximations on the "best theory" that are consistent with the approximations of the calculation. Figure 1 summarizes this approach.

2. Method of Calculation

2.1. The "Best Theory"

Let $\alpha, \beta, \gamma, \ldots$ denote core type Atomic Orbitals (AO's), $i, j, k, \ldots$ valence AO's and $\mu, \nu, \lambda, \ldots$ either. An examination of minimum basis set STO calculations indicates that core and valence AO's cannot be considered as two orthogonal and non-interacting sets. However, we note that

$$\varepsilon_\alpha \approx F_{\alpha\alpha} \tag{1}$$

where $\boldsymbol{F}$ is the Fock energy matrix. This suggests a basis transformation in which the core orbitals remain as they were, but the valence orbitals are Schmidt orthogonalized to all core AO's[1].

$$\begin{aligned} \chi'_\alpha &= \chi_\alpha \\ \chi'_i &= \Big(\chi_i - \sum_\alpha \Delta_{i\alpha}\chi_\alpha\Big)\Big/\Big(1 - \sum_\alpha \Delta_{i\alpha}\Delta_{\alpha i}\Big)^{1/2} \\ \Delta_{i\alpha} &= \langle i|\alpha\rangle = \int d\tau\, \chi_i\chi_\alpha . \end{aligned} \tag{2}$$

With this transformation, the two sets (valence and core) are orthogonal, and have been demonstrated to be nearly non-interacting [1].

Assuming that all valence orbitals are orthogonalized to all core orbitals, we derive our "best theory" utilizing the following approximations.

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[1] Equation (1) also suggests that second order effects in a perturbation treatment will be of minor importance.

Table 1. Atomic parameters

	Li	Be	B	C	N	O	F
g	0.9980	0.9974	0.9961	0.9952	0.9947	0.9942	0.9939
$(1s'2s'/1s'2s')$[a]	0.0131	0.0238	0.0355	0.0468	0.0584	0.0703	0.0820 a.u.
$(1s'2p'/1s'2p')$[a]	0.0045	0.0085	0.0129	0.0173	0.0218	0.0264	0.0310 a.u.

[a] These values are obtained by orthogonalizing the $2s'$ AO to the $1s$, and for STO's with exponents obtained by Slater's rule.

(1) Coulomb repulsion integrals between core and valence orbitals are given by

$$\begin{aligned}(\alpha\alpha|ij) &= \int \chi_\alpha(1)\,\chi_\alpha(1)\,\frac{1}{r_{12}}\,\chi_i(2)\,\chi_j(2)\,d\tau(1)\,d\tau(2)\\ &= \int \chi_i(2)\,\frac{1}{R_{\mathrm{A}}}\,\chi_j(2)\,d\tau_2 \equiv \left(i\left|\frac{1}{R_{\mathrm{A}}}\right|j\right) \quad \alpha\in\mathrm{A}\,.\end{aligned} \tag{3}$$

This is a fairly accurate approximation, the error being of the order $e^{-2\varrho}$, $\varrho = 1/2(\zeta_c + \bar{\zeta}_v)$, ζ_c and $\bar{\zeta}_v$ being the exponent of the core orbital and the average of the two valence orbitals respectively.

(2) a) The charge distribution $\chi_i'(1)\,\chi_\alpha'(1)\,d\tau(1)$ where it appears in multicenter integrals is approximated by zero. The reason for the core orthogonalization is to make this nearly so. Where this distribution occurs in one center exchange integrals, the value of the integral will be set to the free atom value. Some of these integrals are tabulated in Table 1.

b) The charge distribution

$$\chi_i'(1)\,\chi_j'(1)\,d\tau(1) \approx g_{ij}\,\chi_i(1)\,\chi_j(1)\,d\tau(1)$$

where it occurs in integrals. When $g_{ij} = 1$, this is a consequence of Approximation (2a). We will set all $g_{ij} = 1$ except where it occurs in one center integrals. For one center integrals we force the approximation to be nearly so by adjusting g_{ii} accordingly for isolated atoms,

$$\begin{aligned}g_{ii} &= (\alpha\alpha|i'i')/(\alpha\alpha|ii) \approx (\alpha\alpha|i'i')/(i|1/R|i)\\ &= n_i(\alpha\alpha|i'i')/\zeta_i\,.\end{aligned}$$

These values appear in Table 1, and do not differ greatly from unity.

c) Diagonal elements of the density matrix for core elements are set equal to two

$$P_{\alpha\alpha} = 2\,.$$

This is a consequence of the core orthogonalization, and is examined in Ref. [1].

(3) Multicenter integrals which involve differential overlap between two different core orbitals we set to zero,

$$\chi_\alpha(1)\,\chi_\beta(1)\,d\tau_1 = \delta_{\mathrm{AB}}\,\chi_\alpha(1)\,\chi_\beta(1)\,d\tau_1 \quad \begin{matrix}\alpha\in\mathrm{A}\\ \beta\in\mathrm{B}\,.\end{matrix}$$

χ_α and χ_β are so contracted, that this is very nearly so.

(4) The nuclear attraction integrals for core orbitals are approximated by

$$(\alpha|1/R_{\mathrm{B}}|\alpha) \approx 1/R_{\mathrm{AB}} \qquad \alpha \in \mathrm{A} \neq \mathrm{B}\,.$$

The error is of the order of $\exp(-2\varrho)/R$ (where $\varrho = \zeta_c R$), and is quite small as ζ_c is large.

These approximations yield for closed shell molecules in which χ_α is a $1s$ orbital,

$$\begin{aligned}\varepsilon_\alpha \approx F_{\alpha\alpha} = {} & (\alpha'|-1/2\,\nabla^2 - Z_{\mathrm{A}}/R_{\mathrm{A}}|\alpha') + \sum_{\sigma,\lambda} P'_{\sigma\lambda}[(\sigma'\lambda'|\alpha'\alpha') - 1/2(\sigma'\alpha'|\lambda'\alpha')] \\ & - \sum_{\mathrm{B}\neq\mathrm{A}} (\alpha'|Z_{\mathrm{B}}/R_{\mathrm{B}}|\alpha')\,,\end{aligned} \tag{4}$$

$$\begin{aligned}\varepsilon_\alpha \approx {} & \frac{\zeta_\alpha^2}{2} - Z\zeta_\alpha + 0.625\,\zeta_\alpha - \sum_{\mathrm{B}\neq\mathrm{A}} Z^v_{\mathrm{B}}/R_{\mathrm{AB}} - 1/2 \sum_{i\in\mathrm{A}} P'_{ii}(\alpha' i'|\alpha' i') \\ & + \sum_{i,j} P'_{ij} g_{ij} \left(i\left|\frac{1}{R_{\mathrm{A}}}\right|j\right) \qquad \alpha \in \mathrm{A}\end{aligned} \tag{5}$$

$$P_{\sigma\lambda} \equiv 2 \sum_a C_{\sigma a} C_{\lambda a}\,.$$

Z_{A} is the atomic number of atom A, while Z^v_{A} are the number of valence electrons of atom A. Equation (5) is not sensitive to reasonable choices of ζ_α. We set $\zeta_\alpha = Z - 0.3$ for the first row atoms of this study. Assuming a minimum basis set, Eq. (5) becomes

$$\varepsilon_\alpha \approx \frac{\zeta_\alpha^2}{2} - Z\zeta_\alpha + 0.625\,\zeta_\alpha - 1/2 \sum_i n_i(\alpha' i'|\alpha' i') + g(n_s\zeta_s + n_p\zeta_p)/2 \tag{6}$$

with n_s and n_p the number of s and p electrons in the valence shell respectively.

The results of Eq. (6) appear as row 2 in Table 2 where they are compared with eigenvalues obtained from atomic calculations near the Hartree-Fock limit [7]. When compared with minimum basis set calculations using similar exponents, Eq. (6) is nearly exact.

For second row elements, Eq. (4) becomes

$$\begin{aligned}\varepsilon_{1s} \approx {} & \frac{\zeta_1^2}{2} - \zeta_1 Z + 0.625\,\zeta_1 - \sum_{\mathrm{B}\neq\mathrm{A}} Z^v_{\mathrm{B}}/R_{\mathrm{AB}} - 1/2 \sum_{i\in\mathrm{A}} P'_{ii}(1s', i'|1s', i') \\ & + \sum_{i,j} P'_{ij} g_{ij} (i|1/R_{\mathrm{A}}|j)\,,\end{aligned} \tag{7a}$$

$$\begin{aligned}\varepsilon_{2s} \approx {} & \frac{\zeta_2^2}{6} - \frac{\zeta_2(Z-2)}{2} + 2.3021\,\zeta_2 - \sum_{\mathrm{B}\neq\mathrm{A}} Z^v_{\mathrm{B}}/R_{\mathrm{AB}} - 1/2 \sum_{i\in\mathrm{A}} P'_{ii}(2s', i'|2s', i') \\ & + \sum_{i,j} P'_{ij} g_{ij} (i|1/R_{\mathrm{A}}|j) - \Delta^2_{1s\,2s}\varepsilon_{1s}\,,\end{aligned} \tag{7b}$$

$$\begin{aligned}\varepsilon_{2p} \approx {} & \frac{\zeta_2^2}{2} - \frac{\zeta_2(Z-2)}{5} + 2.3924\,\zeta_2 - \sum_{\mathrm{B}\neq\mathrm{A}} Z^v_{\mathrm{B}}/R_{\mathrm{AB}} - 1/2 \sum_{i\in\mathrm{A}} P'_{ii}(2p', i'|2p', i') \\ & + \Sigma\, P'_{ij} g_{ij} (i|1/R_{\mathrm{A}}|j)\,,\end{aligned} \tag{7c}$$

$$\Delta^2_{1s\,2s} = 3/4(1+\tau)^3\,(1-\tau)^5$$

$$\tau = (\zeta_1 - \zeta_2)/(\zeta_1 + \zeta_2)\,.$$

Table 2. Core ionization potentials, first row atoms (a.u.)

	Li	Be	B	C	N	O	F
ε_{1s}[a] (H.F.)	-2.4777	-4.7327	-7.6953	-11.3255	-15.6290	-20.6686	-26.3836
Eq. (6)[b]	-2.4579	-4.7176	-7.6798	-11.3041	-15.5956	-20.6183	-26.3077
Eq. (7)	-2.360	-4.691	-7.689	-11.353	-15.684	-20.680	-26.343
ESCA[c]	2.02	4.08	6.91	10.44	14.66	19.55	25.21
Δ[d]	0.458	0.653	0.785	0.886	0.969	1.119	1.173

[a] Hartree-Fock calculations of atoms, Ref. [7].
[b] Using exponents from Ref. [34].
[c] Reference [2].
[d] $\Delta \equiv -\text{ESCA} - \varepsilon_{1s}(\text{H.F.}) \equiv$ "Relaxation Energy".

Here we have assumed that all orbitals in the L shell can be represented by a single exponent, ζ_2. Since the core orbitals of one center interact very slightly with the cores of other centers, the only term we keep in the core pseudo-potential is the one center repulsion arising from Eq. (2), and appearing in Eq. (7b) as $\Delta^2_{1s\,2s}\varepsilon_{1s}$.

For atoms Eq. (7) become

$$\varepsilon_{1s} \approx \zeta_1^2/2 - \zeta_1 Z + 4\zeta_2 + 0.625\zeta_1 + g(n_{3s}\zeta_{3s} + n_{3p}\zeta_{3p})/3 - 1/2 \sum_i{}^{*} n_i(1s, i' \,|\, 1s, i')$$

$$\begin{aligned} \varepsilon_{2s} = \zeta_2^2/6 - \zeta_2(Z-2)/2 + 2.3021\zeta_2 + g(n_{3s}\zeta_{3s} + n_{3p}\zeta_{3p})/3 - 3/4(1+\tau)^3(1-\tau)^5\,\varepsilon_{1s} \\ - 1/2 \sum_i{}^{*} n_i(2s', i' \,|\, 2s', i') \qquad (8) \end{aligned}$$

$$\varepsilon_{2p} = \zeta_2^2/2 - \zeta_2(Z-2)/2 + 2.3924\zeta_2 + g(n_{3s}\zeta_{3s} + n_{3p}\zeta_{3p})/3 - 1/2 \sum_i{}^{*} n_i(2p, i' \,|\, 2p, i').$$

In Eq. (8) Σ^* designates a sum over all orbitals of shells *other* than the one of interest, and the orbitals met in the sum are orthogonalized to orbitals of all inner shells.

Equations (5)–(8) involve the density of the valence shell only, and these we will call our "best theory". They may be implemented by considering the atomic orbital basis set as orthogonalized to all core orbitals (those not explicitly considered). They are appropriate for use with STO's or LTO's and will yield the same results providing, of course, the corresponding Fock-Dirac density is used.

To check the accuracy of these equations we take exact calculations, calculate the inner shell — outer shell overlap, and core orthogonalize the valence shell. With this new density we use Eq. (5) to calculate the inner-shell eigenvalues, which we compare with the values obtained from the complete calculation. The nuclear attraction integrals that occur in the formulae are obtained utilizing Stewart's [8] three term Gaussian expansions of STO's, and evaluating the one center integrals analytically by

$$(\mu \,|\, 1/R \,|\, \mu) = \zeta_\mu / n_\mu .$$

This has been found to give results very similar to those obtained utilizing Stewart's five term expansion [9], but the former is, of course, more expedient.

A comparison of results for several molecules occurs in Table 3. The agreement is very satisfactory, the estimated values having a rms error of approximately 0.01 a.u.

2.1. *Approximate Formulations*

We now ask if we can simplify our "best theory" using approximations common in semi-empirical molecular orbital theory. To check these approximations independent of the molecular model, we use the core orthogonalized Fock-Dirac density from *ab-initio* calculations, comparing the results with the correctly calculated values. That is, given a good density, is there an easier way to calculate the inner shell eigenvalues?

Referring to the left hand side of Fig. 1, the Mulliken approximation [10] defines differential overlap as

$$\chi_i(1)\,\chi_j(1)\,d\tau = \tfrac{1}{2}\,\Delta_{ij}(\chi_i(1)\,\chi_i(1) + \chi_j(1)\,\chi_j(1))\,d\tau\,. \tag{9}$$

In Method A1, then, (Fig. 1) we utilize the Mulliken approximation, but include in Eq. (5) terms as

$$\text{Polarization} \equiv \sum_{\substack{i \neq j \\ i,j \in \mathrm{B}}} P_{ij}(i\,|\,1/R_{\mathrm{A}}\,|\,j) \tag{10}$$

which would normally vanish if the Mulliken scheme were used for one center differential overlap. We call these terms "polarization" as the integrals are multiplied by the local atomic polarization terms of the density. To maintain rotational invariances, all orbitals are now considered of s type, and only polarization between orbitals of different l value are included. Method A2 differs from A1 by dropping all polarization terms.

If we replace the two center Coulomb integrals that occur in the new equations for A2 by

$$(\alpha\alpha\,|\,ii) \approx (i\,|\,1/R_{\mathrm{A}}\,|\,i) \approx 1/R_{\mathrm{AB}} \qquad \begin{array}{l}\alpha \in \mathrm{A} \\ i \in \mathrm{B} \neq \mathrm{A}\end{array} \tag{11}$$

we arrive at Method A4. Taking differences we derive

$$\varepsilon_{1s}^{\mathrm{mol}} - \varepsilon_{1s}^{\mathrm{atom}} \equiv \Delta\varepsilon_{1s} = g\,\frac{\zeta_2}{n_2}\,q_{\mathrm{A}} + \sum_{\mathrm{B} \neq \mathrm{A}} q_{\mathrm{B}}/R_{\mathrm{AB}} \tag{12}$$

$$q_{\mathrm{A}} = M_{\mathrm{AA}} - Z_{\mathrm{A}}^{v}$$

where $M_{\mathrm{AA}} = \sum_{\mu \in \mathrm{A}} \sum_{\nu} P_{\mu\nu} S_{\nu\mu} \equiv$ Mulliken Atomic Population.

This is the popular charge potential model [2] utilizing Mulliken net charges [10]. Given in its usual form

$$\Delta\varepsilon_{1s} = k_{\mathrm{A}} q_{\mathrm{A}} + b_{\mathrm{A}} \sum_{\mathrm{B} \neq \mathrm{A}} q_{\mathrm{B}}/R_{\mathrm{AB}} + l_{\mathrm{A}} \tag{13}$$

where k_A, b_A, and l_A are empirical factors fitted to experimental values, and are characteristic of Atom A [11]. Derived in this fashion, the shortcomings are those inherent in the Mulliken integral approximation itself, the dropped polarization terms, and the integral approximation of Eq. (11). The latter two approximations are sufficiently severe that only Method A1 seems of interest. Numerical precision is bad, but most trends are maintained.

Approximations common with LTO basis sets are introduced on the right side of Fig. 1. The first of these, Neglect of Differential Diatomic Overlap (NDDO) allows us to drop all three center integrals (as did the Mulliken approximation when we were using STO's). We might then drop two center polarization, as in Intermediate Neglect of Differential Overlap (INDO), or replace integrals between LTO's with the much simpler STO integrals as is done in the popular INDO and CNDO/2 molecular orbital methods [12]. An examination of STO and LTO integrals indicates that reducing the polarization term calculated with STO integrals and LTO densities corrects for the mixed representation. We thus reduce all polarization terms by 0.3 when they occur between orbitals of different l value.

Table 3. Inner shell eigenvalues from *ab-initio* densities (a.u.)

Compound	*Ab-initio*[a]	"Best-Theory"	B2	B4	A4
C_2	-11.365[b,d]	-11.353	-11.322	-11.314	-11.223
H_2CO	-11.357[f]	-11.348	-11.325	-11.296	-11.177
CO	-11.353[d]	-11.354	-11.321	-11.290	-11.261
HCN	-11.335[c]	-11.323	-11.331	-11.291	-11.182
C_2H_2	-11.296[b,c]	-11.286	-11.228	-11.223	-11.183
C_2H_4	-11.287[b,c]	-11.282	-11.209	-11.205	-11.096
C_2H_6	-11.279[b,c]	-11.279	-11.184	-11.182	-11.063
CH_4	-11.271[c]	-11.266	-11.164	-11.164	-11.050
N_2	-15.721[b,c]	-15.728	-15.689	-15.644	-15.509
NO	-15.650[e]	-15.649	-15.632	-15.604	-15.536
HCN	-15.647[c]	-15.655	-15.576	-15.566	-15.424
NH_3	-15.523[c]	-15.520	-15.432	-15.432	-15.303
CO	-20.706[d]	-20.715	-20.741	-20.686	-20.406
NO	-20.623[e]	-20.650	-20.633	-20.596	-20.440
H_2CO	-20.589[f]	-20.600	-20.547	-20.538	-20.385
$\bar{R}$[g]	1.000	0.993	0.973	0.984	0.727
σ	—	0.010	0.061	0.072	0.192

[a] All calculations are minimum basis set.

[b] Average of the core eigenvalues, none differing by more than 0.002 a.u.

[c] Reference [36].

[d] Reference [37].

[e] Reference [38].

[f] Reference [39].

[g] Linear correlation factor, $\bar{R} = (n_C R_C + n_N R_N + n_O R_O)/(n_C + n_N + n_O)$. n_C = number of carbon atoms, R_C the linear correlation factor for carbon centers, etc. R_O is usually much lower than R_C and R_N.

As indicated in Fig. 1, we have tried both orders of approximation, dropping polarization being much more severe than adopting the mixed representation.

If we now make the integral approximation Eq. (11) we derive Eq. (12) again, the charge potential model, but with the charges now calculated from the diagonal terms of the LTO density. To maintain rotational invariances in B5, all integrals are evaluated assuming s type AO's. Method B3 is not invariant to molecular orientation, but the effect of this invariance is not large.

The approximate methods, where they are of sufficient numerical interest, are included in Table 3. B2 and B4 show systematic errors: differences between eigenvalues for similar atoms are generally estimated 60% too great. As B5 is considerably more accurate than B3, we surmise a cancellation of some of the errors introduced by dropping polarization by replacing LTO with STO integrals. The charge potential model, neither with Mulliken (A4) nor LTO (B6) charges, reliably reproduces inner shell eigenvalues. We include the better of these, A4, for comparison.

3. "Valence-Orbital only"-Calculations

In the previous section we have examined methods of obtaining inner shell eigenvalues when the valence density was accurate and the corresponding inner shell eigenvalues for these densities were already known. The more germane problem is to calculate these eigenvalues from approximate calculations in which explicit consideration of the core is lacking, and the accuracy of the density uncertain.

We focis our attention on the following models:

a) INDO/1: Intermediate Neglect of Differential Overlap, assumedly with a near LTO basis and with well defined integral approximation. INDO/1 differs from the INDO method of Pople and coworkers [12c] in obtaining one center core integrals from ionization potentials, and not ionization potentials and electron affinities [13][2].

b) EH and IEH: Extended Hückel [14] and Iterative Extended Hückel [15–17] methods as example of simple calculations with an STO basis.

c) AAMOM: An Approximate Molecular Orbital Method developed by one of us (M.C.Z.) assumedly with a core orthogonalized set of STO's and with well defined integral approximations [18]. AAMOM is constructed in a fashion similar to the method we here outline as B2. Briefly, the two electron part of the Fock matrix is evaluated utilizing the LTO density and integrals over STO-AO's. The two electron matrix is then simplified by neglecting differential diatomic overlap, but corrects for missing three center terms through a model potential.

Part of the results of this investigation are given in Tables 4 and 5 where we compare estimated core eigenvalues and linear correlation factors R_i, from attempting simple linear fits of the form

$$\varepsilon(\textit{ab-initio}) = m_i \varepsilon(\text{estimated}) + \varepsilon_i^0$$

where the subscript i refers to different type atoms. When the correlation is near unity, the estimate shows predictive promise. When the factor is much less than

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[2] Preliminary calculation with INDO/2 have indicated INDO/1 more adequate.

Table 4. Core eigenvalues from approximate valence methods (a.u.)

Compound	*Ab-Initio*[a]	INDO/1 (B6)	AAMOM (B2)
CO_2	-11.534^f	-11.438	-11.491
C_2	-11.365^b	-11.223	-11.324
H_2CO	-11.357^e	-11.287	-11.305
CO	-11.353^b	-11.225	-11.340
HCN	-11.335^c	-11.227	-11.284
$H_3\overset{*}{C}CN$	$(-11.308)^d$	-11.216	-11.279
$H_3CC\overset{*}{N}$	$(-11.300)^d$	-11.231	-11.289
C_2H_2	-11.296^c	-11.165	-11.229
C_2H_4	-11.287^c	-11.170	-11.222
C_2H_6	-11.279^c	-11.170	-11.211
CH_4	-11.271^c	-11.144	-11.195
$NN\overset{*}{O}$	$(-15.840)^g$	-15.797	-15.877
N_2	-15.721^b	-15.509	-15.682
$\overset{*}{N}NO$	$(-15.695)^g$	-15.488	-15.603
HCN	-15.647^c	-15.423	-15.591
H_3CCN	$(-15.597)^d$	-15.372	-15.543
NH_3	-15.523^c	-15.326	-15.438
$O\overset{*}{O}O$	-20.834^h	-20.710	-20.845
CO	-20.706^b	-20.475	-20.667
NNO	$(-20.651)^g$	-20.288	-20.546
F_2O	-20.618^h	-20.598	-20.640
H_2CO	-20.589^e	-20.330	-20.573
CO_2	-20.584^f	-20.344	-20.578
H_2O	-20.556^i	-20.275	-20.420
OOO^*	-20.547^h	-20.391	-20.511
R^j (calc)	1.000	0.943	0.974
σ^k	--	0.17	0.06
σ^l (fit)	--	0.04	0.02

[a] Values in parenthesis are not from minimum basis set calculations.
Reference [37]. [c] Reference [36]. [d] Reference [40]. [e] Reference [39].
[f] Reference [41]. [g] Reference [42]. [h] Reference [43]. [i] Reference [44].
[j] See Footnote [g]), Table 3.
[k] The standard deviation between *ab-initio* and estimated.
[l] The standard deviation obtained using the least squared linear relationship between *ab-initio* and estimated.

~0.9, we do not consider the fit very good. Not to be misled by such an analysis, we have successively dropped end points from the data to insure no great deterioration in R_i.

An examination of INDO results indicates that Methods B6 and B5 are best in reproducing core eigenvalue trends ($\bar{R} = 0.94$). These methods are variants

Table 5. Adenine eigenvalues (a.u.)

Atom[a]	*Ab-Initio*		AAMOM		INDO/1	EH	ESCA[e]
			"Best"	B2	B6	A1	
N(9)	−15.760[b]	−15.897[c]	−15.780	−15.711	−15.502	−15.687	−14.733
N(10)	−15.654	−15.792	−15.663	−15.591	−15.404	−15.408	−14.686
N(8)	−15.650	−15.791	−15.595	−15.513	−15.338[g]	−15.016[g]	−14.682
N(7)	−15.640	−15.774	−15.572	−15.488	−15.346	−15.078	−14.667
N(6)	−15.635	−15.771	−15.561	−15.475	−15.341	−15.056	−14.649
range	0.125	0.126	0.219	0.236	0.164	0.671	0.084
C(4)	−11.534	−11.556	−11.430	−11.358	−11.287	−11.554[g]	−10.577
C(2)	−11.511	−11.537	−11.375	−11.322	−11.275	−11.593	−10.533
C(5)	−11.491	−11.517	−11.350[g]	−11.303	−11.253	−11.632	−10.518
C(1)	−11.482	−11.503	−11.360	−11.288	−11.239	−11.507	−10.500
C(3)	−11.437	−11.463	−11.247	−11.224	−11.209	−11.465	−10.463
range	0.097	0.093	0.183	0.134	.078	0.167	0.114
R_{calc}[d]	1.000	0.998	0.973	0.986	0.970	0.753	0.961
R_{exp}[d]	0.961	0.965	0.965[f]	0.980	0.944[f]	0.722[f]	1.000

[a] Atom numbering as in Fig. 2.

[b] Clementi, E. [25].

[c] Pullman, A. [45].

[d] Correlation factor, R_{calc} relative to calculation *A*, $R = (R_C + R_N)/2$ where the C and N eigenvalues are correlated separately.

[e] Reference [20].

[f] Fitted as if *ab-initio* assignment of spectrum is correct.

[g] Brackets denote reversals from *ab-initio* ordering.

of the charge potential model with symmetrically orthogonalized charges (LTO). Neither of these methods are qualitatively correct when applied to the two centers of a diatomic molecule. Because of charge neutrality these methods predict that the eigenvalue associated with one center will shift up while the other shifts down relative to atomic values, and that homonuclear diatomics will show no shift at all. Both of these conclusions have been shown by experiment and by calculation to be incorrect. The more sophisticated models that we have tried, and that are qualitatively correct for diatomics, show a very poor overall predictive power. That our "best theory" is rather unsuccessful ($R_C = 0.71$, down from 0.94 upon dropping the extreme carbon of CO_2) sheds some doubt on the LTO basis assumed for INDO/1; that B5 shows success is some indication that a consistent treatment of integrals does give definition to the unspecified basis.

We have not been able to find any theory which accurately extracts inner-shell eigenvalues from the Extended Hückel model. (See, however, Schwartz, Switalski, and Stronski [11] who employ an empirical method.) The iterative procedure does not seem to improve these results: carbon deteriorates, showing little predictive strength, while oxygen improves. For non-polar molecules as, for example, the series CH_4, C_2H_2, C_2H_4, C_2H_6, C_2, both EH and IEH work reasonably well with the A1 method.

Inner-shell eigenvalues seem best extracted from AAMOM. Although the "Best Theory" gives absolute values in good agreement with core-eigenvalues

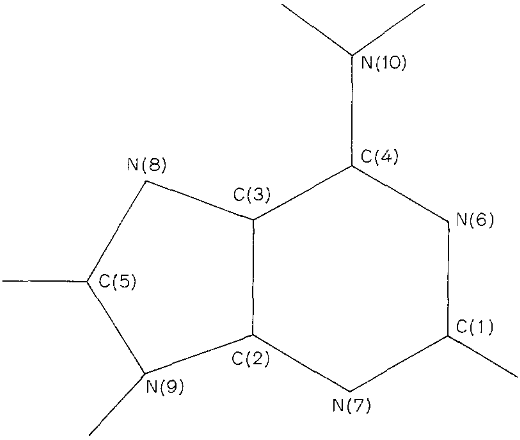

Fig. 2. Adenine

calculated directly from *ab-initio* studies, methods B2 ($\bar{R} = 0.97$) and B4 ($\bar{R} = 0.95$) with integral approximations consistent with AAMOM itself have the better correlations. Method A1 also reproduces eigenvalue trends ($\bar{R} = 0.93$), whereas lower level approximations are not as reliable.

Experimentally there is, of course, no difficulty in separating ionization processes for different molecules. Since we wish to compare inner-shell eigenvalues with experimental ESCA, the problem of greater interest is to examine intramolecular shifts of atoms caused by different chemical environments. Several examples are given of intramolecular shifts for small molecules in Table 4. Table 5 presents the information for the largest molecule we have examined, adenine, Fig. 2. (Adenine has also been examined by Rein, Hartman, and Nir [19] and Barber and Clark [20].)

4. Ionization Spectra (XPS)

4.1. Comparison with Eigenvalues

In the previous sections we have developed several theories capable of producing core eigenvalues from calculations which do not explicitly contain core electrons. Can these eigenvalues then be used to explain the corresponding numbers from experimental XPS? Much attention has been given to this question [11, 21–24] with the general conclusion that if the calculations are "good enough", they can be used to assign the experimental lines. Indeed, this has become the principal method of assigning the several lines that are obtained from a single molecular species.

Below we briefly analyze the correlation we find between our estimated eigenvalues and experimental XPS. For the several lines that appear for a single molecular species, we *assume* the order implied by the *ab-initio* calculations. We further assume as best those methods which have the greatest average linear correlation factor $\bar{R} = (n_C R_C + n_O R_O + n_N R_N)/(n_C + n_O + n_N)$. When correlations are similar we give preference to methods which distinguish best intra-molecular ionization processes.

The comparison between *ab-initio* eigenvalues and experiment was done for 26 atomic centers: that between the approximate methods and experiment, for 45 centers.

Minimum basis set *ab-initio* eigenvalues correlate reasonably well with ionization potentials for carbon and nitrogen atoms ($R_{C+N} = 0.92$). If we include the ten intra-molecular ionization processes of adenine [25] assuming the experimental order is the calculated one, the correlation is slightly improved ($R_{C+N} = 0.94$). The eigenvalues of *ab-initio* minimum basis set calculations, however, do not appear to accurately reproduce the ionization potentials of processes localized to oxygen atoms ($R_O = 0.72$). This situation is not very much improved when we consider calculations of near Hartree-Fock accuracy ($R_O = 0.83$) (see, for example, Table 6). The molecules most out of line appear to be aldehydes and, for the more accurate calculations, H_2O.

Table 6. Comparison of calculated and experimental ESCA shifts (eV)[a]

	Raw Data				Fitted				
Compound	*Ab Initio*	INDO/1		AAMOM	*Ab Initio*	INDO/1		AAMOM	Exp.
		B6	A4	B2		B6	A4	B2	
CF_4		13.25	18.09	12.79		11.33	11.22	11.59	11.00[b]
CO_2	7.16	8.00	12.03	8.05	7.82	6.88	7.33	7.19	6.84[b]
CO	2.23	2.20	5.69	3.94	2.67	1.91	3.30	3.43	5.40[b]
$HCOOH$		5.63	7.35	5.25		4.82	4.32	4.63	4.99[b]
$CH_3\overset{*}{C}OOH$		5.63	8.22	5.09		4.82	4.90	4.53	4.70[e]
H_2CO	2.34	2.89	5.74	2.99	2.78	3.37	3.30	2.61	3.30[e]
$CH_3\overset{*}{C}HO$		3.73	5.88	3.10		3.20	3.43	2.70	3.20[e]
HCN	1.74	2.26	4.54	2.42	2.15	2.00	2.54	2.06	2.60[b]
$CH_3\overset{*}{C}N$		2.37	4.68	2.56		2.08	2.66	2.24	2.10[d]
$\overset{*}{C}H_3CN$		1.96	2.53	2.28		1.74	1.26	1.97	2.10[d]
CH_3OH		2.20	2.96	2.48		1.91	1.58	2.15	1.90[b]
$CH_3\overset{*}{C}H_2OH$		2.72	3.62	2.77		2.34	1.96	2.43	1.60[e]
$\overset{*}{C}H_3COOH$		1.22	1.88	1.20		1.06	0.88	0.96	0.70[e]
$\overset{*}{C}H_3CHO$		1.39	1.96	1.06		1.23	0.94	0.87	0.60[e]
C_2H_2	0.68	0.57	1.85	0.92	1.10	0.54	0.81	0.68	0.40[c]
$\overset{*}{C}H_3CH_2OH$		0.90	1.22	0.92		0.80	0.43	0.68	0.20[e]
CH_4	0.00	0.00	0.00	0.00	0.36	0.03	-0.34	-0.14	0.00[b]
C_2H_4	0.44	0.71	1.33	0.73	0.78	0.63	0.49	0.50	-0.10[c]
C_2H_6	0.22	0.71	0.98	0.44	0.57	0.63	0.30	0.23	-0.20[c]
σ[g]					1.25	0.90	0.63	0.62	
R					.890	.947	.974	.975	
A[h]					1.050	.856	.639	.916	
B[h]					.363	.028	-.337	-.140	

Table 6 (continued)

Compound	Ab Initio	Raw Data INDO/1		AAMOM	Ab Initio	Fitted INDO/1		AAMOM	Exp.
		B6	A4	B2		B6	A4	B2	
$\mathrm{NN\overset{*}{O}}$		7.84	6.80	5.30		3.12	2.63	2.86	2.60[e]
N_2	0.00	0.00	0.00	0.00	0.10	-1.03	-0.64	-0.38	0.00[e]
HCN	-2.01	-2.34	-3.89	-2.48	-1.50	-2.27	-2.50	-1.89	-1.30[e]
$\mathrm{\overset{*}{N}NO}$		-0.57	0.16	-2.15		-1.33	-0.56	-1.69	-1.40[e]
CH_3CN		-3.73	-4.87	-3.78		-3.01	-2.98	-2.69	-3.80[f]
NH_3	-5.39	-4.98	-7.26	-6.64	-4.20	-3.67	-4.12	-4.44	-4.38[e]
σ[g]						0.81	0.71	0.61	
R						.948	.947	.972	
A[h]						.530	.480	.611	
B[h]						-1.030	-.638	-.379	
CO	4.08	5.44	4.08	6.72	2.77	3.03	2.94	2.73	2.94[b]
NNO		0.35	2.01	3.43		0.17	1.30	0.92	1.54[b]
CO_2	0.76	1.9	2.3	4.30	0.17	1.03	1.54	1.42	1.44[b]
$\mathrm{CH_3CO\overset{*}{O}H}$		1.77	0.98	3.10		0.97	0.53	0.76	0.74[e]
$\mathrm{HCO\overset{*}{O}H}$		2.01	1.36	3.48		1.08	0.84	0.98	0.67[b]
H_2O	0.00	0.00	0.00	0.00	-0.46	-0.06	-0.25	-0.94	0.00[b]
CH_3CH_2OH		-0.60	-0.92	0.08		-0.40	-0.95	-0.88	-0.66[e]
CH_3OH		-0.33	-0.71	0.24		-0.23	-0.80	-0.83	-0.80[b]
$\mathrm{HC\overset{*}{O}OH}$		-0.82	0.03	1.63		-0.52	-0.25	-0.06	-0.95[b]
$\mathrm{CH_3C\overset{*}{O}OH}$		-1.99	-0.98	1.28		-1.20	-1.03	-0.23	-1.06[e]
H_2CO	0.90	(1.50)	(1.25)	(4.16)	0.25	(0.80)	(0.68)	(1.36)	-1.66[e]
CH_3CHO		(0.03)	(0.08)	(3.29)		(-.06)	(-.17)	(0.87)	-1.66[e]
σ[g]						0.56	0.29	0.57	
R						.903	.975	.902	
A[h]						.572	.778	.548	
B[h]						-.060	-.252	-.940	

[a] Reference compounds: CH_4 for carbon, N_2 for Nitrogen, H_2O for oxygen. For absolute values see Table 4 [INDO/1 (A4) $CH_4 = 302.7$ eV, $N_2 = 422{,}0$ eV, $H_2O = 549.9$ eV].

[b] Reference [47].

[c] Reference [46].

[d] Reference [48].

[e] Reference [3].

[f] Reference [40].

[g] $\sigma = \sqrt{\frac{(\varepsilon_{\text{calc}} - \varepsilon_{\text{exp}})^2}{n-1}}$.

[h] Δ (estimate) $= A_i(\varepsilon_i(\text{approx}) - \varepsilon_i^{\text{ref}}(\text{approx})) + B_i$; for carbon the reference eigenvalue is CH_4, for nitrogen N_2 and for oxygen H_2O. See a.

For comparison, the core-eigenvalues published by Basch and Snyder [26] which have the advantage of all being calculated at the same level of sophistication (double ζ) yield a correlation for carbon of $R_C = 0.98$, but for oxygen, $R_O = 0.90$. Here, again, both H_2CO and H_2O are poorly treated. Their neglect in the "fit" brings the correlation between calculation and experiment for oxygen to $R_O = 0.95$. We have found the aldehyde oxygens poorly treated in nearly every model examined. For this reason, the aldehyde oxygens have been removed from the following comparisons.

Within the INDO/1 model Method A4 gives eigenvalues that correlate well with experimental XPS ($\bar{R} = 0.96$), although differences (shifts) are exaggerated. It is remarkable that eigenvalues estimated for oxygen atoms by INDO compare better with XPS [$R_O(\text{A4}) = 0.98$, $R_O(\text{B6}) = 0.90$] than they do with the corresponding *ab-initio* eigenvalues [$R_O(\text{A4}) = 0.67$, $R_O(\text{B6}) = 0.83$]. The oxygen atoms from INDO studies are found to be 0.1–0.2 electrons richer than in the corresponding *ab-initio* calculations. Perhaps the semi-empirical fitting of parameters corrects for difficiencies in the minimal basis set *ab-initio* model.

Method A4 is the charge potential model of Siegbahn and co-workers [2, 3], but the Fock-Dirac density is deorthogonalized, and Mulliken charges are used. It is not consistent with the philosophy behind the INDO model *per se*. The method showing the greatest promise utilizing the resultant LTO density directly is B6, the charge potential model utilizing "Löwdin" charges. The fit here, however, is relatively poorer ($\bar{R} = 0.94$) than that for A4.

The eigenvalues estimated from EH or IEH do not show much promise of yielding core ionization energies for electrons associated with either carbon or nitrogen. The best overall method is A1 with $\bar{R} = 0.88$. Interestingly enough, the EH model that calculates the largest net charges is one of the more successful theories for electronegative oxygen even when the aldehydes found troublesome with other models (A1 and A3, $R_O = 0.92$).

For AAMOM methods B2 and B4 appear best ($\bar{R} \sim 0.96$). The oxygen atom is again not well treated.

Table 6 summarizes our comparison between estimated and observed ionization shifts for methods with predictive promise. Although differences of less than ~1 eV between ionization potentials for different molecules cannot be assigned with confidence, the order of intra-molecular ionization processes appears distinguished when they are separated by ~0.3 eV (see also, Table 5).

We conclude that minimum basis set *ab-initio* eigenvalues, and those obtained from INDO or AAMOM, can be used to estimate ionization energies from inner shell eigenvalues for orbitals localized on carbon or nitrogen. For orbitals centered on oxygen, the AAMOM and INDO models with semi-empirical atomic parameters show a somewhat greater power of predicting ionization energies than the corresponding minimum basis set *ab-initio* calculations. Since the EH model with the largest charge build up shows the greatest success when applied to oxygen, the lack of electron correlation and a sufficient basis set to accommodate more charge may be important[3].

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[3] Schwartz *et al.*, Ref. [11], use CNDO with some degree of success for fluorine shifts, where the lack of correlation and an adequate atomic basis should have an even larger effect in damaging the quality of the wavefunction. The range of experimental values they studied, though, is not large (four molecules with 1.6 eV range).

4.2. *Discussion*

Koopmans' Approximation is often referred to as a "sudden approximation" – the removal of an electron with no time for the resulting ion to relax and realize its "proper" state. Newton [27] has shown that the negative of these eigenvalues, ε, will usually provide upper bounds for ionized states, implying that ε will be greater than the values obtained by calculating the energy of the ion itself and subtracting. The latter process, representing complete relaxation, when given greater variational freedom, appears to give satisfactory numerical agreement with experiment [28–30] even when both calculations are of the Hartree-Fock type. The implication is that correlation effects nearly cancel, and relativistic corrections now account for the small discrepancy between "ΔE" and the observed ionization processes[4].

The last row of Table 2 demonstates the difference between Koopmans' approximation and the ionization potentials measured from XPS, or relaxation energy, Δ, realized by XPS for first row ions. The relaxation energy is large, and unless we assume that this energy is principally a function of atom type, or, at worst, monotonically dependent on ionization energy, itself ($\Delta_{1s} \approx -0.02387\,\varepsilon_{1s} + 0.58702$ a.u. is a fairly accurate expression), eigenvalues might not provide an accurate guide for the experimental assignments[5].

Noting, however, that the fast moving remaining core electron circles the nucleus several times while the ejected electron is still under the influence of the atom, and the slower valence electrons have not, it is reasonable to assume that most of the relaxation energy is associated with the valence shell contraction caused by a less screened nucleus, and a spin hole. As details of the valence shell are a complex function of the molecule, the failure of Koopman's approximation might be nearly as common as it is for valence shell ionization processes. Koopmans' approximation might thus be an unreliable procedure in assigning near lying lines of an ionization spectrum.

Even accepting for the moment that eigenvalues can be used to assign the relative lines of an XPS experiment, a question that still remains concerns the quality of the calculation. Calculations near the Hartree-Fock limit would seem best for both inter- and intra-molecule comparisons. Minimum basis set calculations, however, might be unreliable. One might expect the eigenvalues from similar calculations on different molecules to reflect trends, but the quality of a wavefunction is not only a function of the truncated basis, but also of the molecule; that is, a minimum basis set calculation will better describe one molecule than another. In a similar fashion calculations far from Hartree-Fock accuracy might treat one part of a molecule more precisely than another. This might be manifest in a poor prediction of bond lengths and other "local" properties in the region of the molecule less accurately treated. This would also lead to an eigenvalue

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[4] Koopmans' approximation and the ΔSCF procedure are reasonably well founded for valence ionized states. For core ionized states the proximity of excited hole states and continua opens both of these procedures to questioning. The numerical evidence, however, suggests both ideas are reasonably sound even in core ionized states, and probably reflect the soundness of the shell structure model [27, 28].

[5] Such a monotonic dependence of relaxation on ionization energy has been recognized for valence shell processes; see, for example, Ref. [31].

ordering in poor agreement with ionization experiment. Nevertheless, it is generally assumed that intra-molecular comparisons can be made with such calculations, even when inter-molecular comparisons cannot. We also have favoured those methods which reproduce intra-molecular spectra at the expense of those more accurately reproducing inter-molecular shifts, should there be a conflict. We do this not on theoretical grounds, but because intra-molecular assignments are experimentally more interesting.

We have found that the eigenvalues for core orbitals centered on carbon and nitrogen in general correlate well with inner-shell ionization energies. This is especially so for calculations of "double ζ" or better quality. For oxygen the correlation is poorer. Minimum basis set calculations that are acceptable in reproducing most trends in molecules containing carbon and nitrogen are poorer for the more electronegative elements where the number of electrons per available orbital is high (less variational freedom), and where electron correlation may be important. Minimum basis set calculations for molecules containing oxygen and fluorine are noted for yielding bond lengths and force constants in much poorer agreement with experiment than similar calculations containing the other atoms of the first row [32].

Finally, we note that the eigenvalues we calculate are not insensitive to the input geometry assumed. Most sensitive of all to geometry are the oxygens of this study. For example, with AAMOM and assuming gas phase coordinates for the carboxylic acids of this study ($R(\mathrm{C{=}O}) = 1.24\,\text{Å}$, $R(\mathrm{C{-}O}) = 1.40\,\text{Å}$, Ref. [33]) give oxygen eigenvalues nearly equal; assuming crystallographic coordinates ($R(\mathrm{C{=}O}) = 1.24\,\text{Å}$, $R(\mathrm{C{-}O}) = 1.29\,\text{Å}$, Ref. [34]) gives eigenvalues split by 1.8 eV, in excellent agreement with ionization energies. No reasonable charge in geometry, however, can be used to explain the observations on formaldehyde and acetaldehyde.

5. Conclusions

Inner shell eigenvalues can be obtained in a relatively straightforward manner from the valence shell density matrix of accurate calculations if we assume the valence shell basis orthogonal to the neglected core. Much simpler methods than our "Best Theory" can be used to extract trends among eigenvalues, but the absolute values obtained are in poorer agreement with the model *ab-initio* results. The AAMOM technique, and, to a lesser extent, the INDO model, can be used to yield core eigenvalues for orbitals centered on carbon and nitrogen. For oxygen the agreement is poorer. We have not been able to find any simple reliable way to reproduce core eigenvalues from the Extended Hückel model, although other have done so utilizing curve fitting procedures to calculated molecular parameter [11].

Eigenvalues from *ab-initio* studies, or those obtained from AAMOM or INDO can be used with some confidence in assigning ionization processes from orbitals localized on carbons and nitrogens. The oxygens are less accurately treated. This may be caused by the relatively poorer treatment that oxygen atoms receive in minimum basis set SCF-MO calculations (see text), that does not allow charge build-up, by failures in Koopmans' approximation, and by the fact that these eigenvalues seem strongly geometry dependent. This latter disadvantage could obviously be turned to interesting advantage could we trust the quality (or consistency) of the minimum basis set SCF-MO models examined.

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