

RELATIVISTICALLY PARAMETERIZED EXTENDED HÜCKEL THEORY

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Received 3 November 1978; in final form 22 December 1978

A relativistically parameterized extended Hückel molecular orbital method is outlined. One-electron effective hamiltonian matrix elements are related to the corresponding overlap matrix elements calculated in an atomic $|lsjm\rangle$ basis. Different atomic radial functions are used for the $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ basis functions for a given n and l . Relativistic and non-relativistic atomic orbital energies are taken from atomic Dirac-Fock and Hartree-Fock calculations. Results are presented for the molecules I_2 , Br_2 , IBr , HI , InI , CH_4 , SiH_4 , GeH_4 , SnH_4 , PbH_4 , $(114)H_4$ and Bi_4 . It is concluded that our method and its parameterization provide a semi-quantitative description of relativistic effects in chemical bonding.

1. Method

The basic assumption of a semi-empirical LCAO MO method of the extended Hückel (EHT) type [1,2] is that matrix elements h_{ij} (for $i \neq j$) of an unspecified one-electron effective hamiltonian h_{eff} are related to the corresponding overlap matrix elements S_{ij}

$$h_{ij} = \langle \psi_i | h_{eff} | \psi_j \rangle = f(h_{ii}, h_{jj}) S_{ij}, \quad (1)$$

where the function $f(h_{ii}, h_{jj})$ is usually expressed in terms of the arithmetic mean of h_{ii} and h_{jj} by

$$f(h_{ii}, h_{jj}) = k(h_{ii} + h_{jj})/2, \quad (2)$$

where the bond constant k is usually assigned a value around 1.75. Input parameters consist of the molecular geometry, a basis set of atomic orbitals, and a set of atomic orbital energy parameters $\{h_{ii}\}$.

In order to obtain semi-quantitative estimates of the bonding properties of molecules containing one or more atoms with large Z , and to obtain a measure of the relativistic contribution to such properties, we have developed a relativistically parameterized version of EHT which we designate as "REX". The key fea-

tures of REX lie in the choice of atomic basis functions and in the choice of atomic orbital energy parameters. First, the overlap matrix elements S_{ij} are calculated with respect to a set of basis functions with an $|lsjm\rangle$ quantization; the procedure for doing this is described in the next section. Second, the $|lsjm\rangle$ functions have associated radial factors obtained by fitting one or more Slater radial functions to the relativistic atomic radial functions of Desclaux [3]. The procedure we have initially used is to choose a single Slater exponent ζ by matching the electron mean radius \bar{r} ;

$$\zeta = (n + \frac{1}{2})/\bar{r}, \quad (3)$$

where n is the principal quantum number. The small component of a valence AO contributes only slightly to \bar{r} and becomes negligibly small in the valence region, compared to the large component. We therefore may relate our two-component Pauli functions directly to Desclaux's four-component \bar{r} values. Since values of \bar{r} are a function of n , l , and j , the corresponding ζ 's differ for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ for a given n and l . Third, all orbital energy parameters $\{h_{ii}\}$ are

taken as the Dirac–Fock orbital energies $\{\epsilon_i\}$. Since Desclaux's tables [3] also include \bar{r} and ϵ values for the Hartree–Fock non-relativistic limit of $c \rightarrow \infty$, we thus have available consistent relativistic ($c = 137.03$ au) and non-relativistic ($c \rightarrow \infty$) parameterizations for the ζ_i and h_{ii} values. We denote these two parameterizations as REX and EHT respectively, where *both* employ the $|lsjm\rangle$ basis. Thus direct comparison of REX and the present EHT treatments for a given molecule provides a direct measure of the importance of relativity. Spin–orbit splittings for atomic orbitals with $l \neq 0$ and relativistic shifts for *all* orbitals, including those with $l = 0$, are thus taken into account without a “spin–orbit” hamiltonian being specified. Molecular effects enter via eqs. (1) and (2). The eigenvalue problem $(H - \epsilon S)c = 0$ is then solved by standard methods, taking into account that matrices H and S are in general complex. These matrices are of dimension $2n \times 2n$, where $2n$ is the number of spin-orbitals.

Our method REX resembles that developed by Manne, Wittel and Mohanty (hereafter referred to as MWM) [4][‡] and applied to a large number of molecules [4–9]. Their interest was primarily in relating MO eigenvalues to ionization energies obtained by photoelectron spectroscopy. Our method is characterized by a more systematic parameterization, including a well-defined relativistic contraction, or expansion for each orbital. Their calculations were constrained by a common radial factor for the atomic orbitals with $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$. Their assumptions [4] about matrix elements (ME's) of an “effective one-electron spin–orbit hamiltonian” h_{so} include neglect of all three-center and certain two-center ME's, evaluation of one-center ME's in terms of empirical spin–orbit parameters, and expansion of two-center ME's involving orbital on center A connected by the component h_{so} on center A to an orbital on center B in terms of one-center (A) ME's.

If the MWM assumptions were applied to our $|lsjm\rangle$ basis, in which the one-center spin–orbit coupling is diagonal, then a two-center ME in a diatomic molecule becomes

$$\langle \psi_i^A | h_{so} | \psi_j^B \rangle = W[(h_{so}^A)_{ii} + (h_{so}^B)_{jj}] S_{ij}, \quad (4)$$

where A and B denote the centers, W is the MWM parameter, and $(h_{so}^A)_{ii}$ denotes a one-center ME for

[‡] This paper contains a thorough discussion of their spin–orbit modified extended Hückel method.

center α . In REX the corresponding ME is

$$\langle \psi_i^A | \Delta h | \psi_j^B \rangle = (k/2)(\Delta\epsilon_i + \Delta\epsilon_j) S_{ij}, \quad (5)$$

where $\Delta h \equiv h^R - h^{NR}$ and $\Delta\epsilon_i \equiv \epsilon_i^R - \epsilon_i^{NR}$ with R and NR denoting the relativistic and non-relativistic parameterizations, respectively. The MWM value of W is 0.5, while $k/2$ is 0.875 suggesting larger two-center ME's with REX. However the $\{\Delta\epsilon_i\}$ include relativistic shifts as well as splittings.

MWM used atomic spin–orbit splittings and ionization potentials from experimental atomic spectra. Thus their results also include the relativistic shifts. A systematic comparison with non-relativistic results is, however, precluded.

Before the present work was completed, we became aware of the rather analogous, iterative, “self-consistent quasi-relativistic modified extended Hückel” method of Boudreaux et al. [10]. A “quasi-relativistic Mulliken–Wolfsberg–Helmholz” method was also discussed by Bersuker et al. [11], while the entire field of relativistic quantum chemistry has been recently reviewed by Pyykkö [12].

2. Calculation of overlap matrix

REX has been written as an adaptation of a standard EHT FORTRAN program[‡]. The overlap matrix S in the $|lsjm\rangle$ basis is readily calculated by supplying as input data *two* sets of real atomic orbitals for each atom. The first and second sets consist of those orbitals whose radial functions are later associated with the $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$ orbitals respectively. Thus for an atom with s, p, and d AO's, the two sets are associated with $s_{1/2}$, $p_{1/2}$, $d_{3/2}$ and $s_{1/2}$, $p_{3/2}$, $d_{5/2}$, respectively. (The s AO is duplicated so that a generalization to spin-polarized orbitals is possible.) The standard EHT routines for calculating the real overlap matrix in a real AO basis are employed. One-center overlap matrix elements connecting the two sets are not calculated, as they are not required. A unitary transformation is then used to obtain S in the desired basis. For example, the three real p AO's of the first set are used to construct the two functions

[‡] The original EHT program was obtained from its author R. Hoffmann in 1966 and is an earlier version of the program recently published [13].

with $j = 1/2$ and $m = \pm 1/2$, while the three real p AO's of the second set are used to construct the four functions with $j = 3/2$ and $m = \pm 3/2, \pm 1/2$. The transformation is based on complex spherical harmonics defined as [14, p. 60]

$$Y_{lm}(\theta, \phi) = N(-1)^{(m+|m|)/2} P_l^{|m|}(\cos \theta) \exp(im\phi), \quad (6)$$

where N is a positive normalization constant dependent on l and m , and on real harmonics defined as [14, p. 200]

$$Z_l = Y_{l0}, \quad (7a)$$

$$Z_{lm}^c = 2^{-1/2} (Y_{l,-m} + \bar{Y}_{l,-m}), \quad (7b)$$

$$Z_{lm}^s = 2^{-1/2} i(Y_{l,-m} - \bar{Y}_{l,-m}). \quad (7c)$$

The phase convention for the $|lsjm\rangle$ basis is expressed in terms of 3- j symbols by [15]

$$|lsjm\rangle = \sum_{m_l, m_s} C(lm_l \frac{1}{2} m_s, jm) |lm_l m_s\rangle \quad (8)$$

and

$$C(lm_l \frac{1}{2} m_s; jm) = (-1)^{1/2-l-m} (2j+1)^{1/2} \begin{pmatrix} l & \frac{1}{2} & j \\ m_l & m_s & -m \end{pmatrix}. \quad (9)$$

The transformation can be carried out separately for each atom-pair block of the original overlap matrix and separately for α and β spins. Thus although formally a $2n \times 4n$ transformation matrix is required, the actual transformations used range from 2×2 for atoms with s AO's only to 32×32 for atoms with s, p, d, and f AO's.

3. Results

Calculated orbital energies for I_2 obtained using the parameters in table 1 and a bond length of 2.67 Å are presented in fig. 1 together with experimental values [16-18] and the theoretical values of Manne et al. [4] and of Yang [19], the latter obtained using a Dirac-Slater multiple scattering $X\alpha$ method. The spin-orbit splitting of the π_g^* MO is somewhat less than that of the π_u MO, in agreement with experiment. These splittings have been discussed in detail

Table 1
REX parameters

Element	Orbital	$-\alpha_i$ (eV)		ξ_i	
		rel.	non-rel.	rel.	non-rel.
H	1s	13.606	13.606	1.000	1.000
C	2s	19.39	19.38	1.577	1.576
	2p _{1/2}	11.07	11.07	1.435	1.435
	2p _{3/2}	11.06	11.07	1.434	1.435
Si	3s	14.84	14.79	1.592	1.588
	3p _{1/2}	7.59	7.58	1.257	1.256
	3p _{3/2}	7.56	7.58	1.254	1.256
Ge	4s	15.52	15.16	2.057	2.024
	4p _{1/2}	7.42	7.33	1.569	1.550
	4p _{3/2}	7.24	7.33	1.544	1.550
Sn	5s	13.88	13.04	2.218	2.129
	5p _{1/2}	7.01	6.76	1.732	1.674
	5p _{3/2}	6.57	6.76	1.664	1.674
Pb	6s	15.42	12.49	2.718	2.386
	6p _{1/2}	7.49	6.53	2.114	1.880
	6p _{3/2}	5.98	6.53	1.848	1.880
114	7s	19.63	-	3.405	-
	7p _{1/2}	9.67	-	2.749	-
	7p _{3/2}	5.02	-	1.892	-
Br	4s	27.78	27.01	2.632	2.588
	4p _{1/2}	12.79	12.44	2.169	2.131
	4p _{3/2}	12.23	12.44	2.124	2.131
I	5s	23.86	22.34	2.731	2.626
	5p _{1/2}	11.72	10.97	2.289	2.198
	5p _{3/2}	10.58	10.97	2.186	2.198
Bi	6s	18.67	15.19	2.898	2.560
	6p _{1/2}	9.21	7.79	2.338	2.072
	6p _{3/2}	7.11	7.79	2.040	2.072

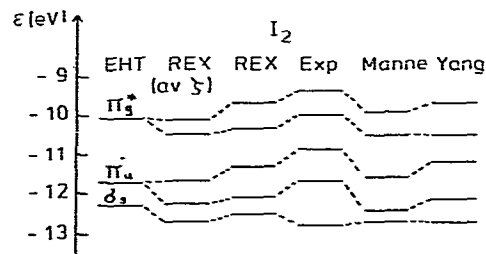


Fig. 1. Calculated non-relativistic (EHT) and relativistic (REX) orbital energies for I_2 . Also shown are the calculated energies of Manne et al. [4] and of Yang [19], and experimental orbital energies [16-18]. The results labeled REX (av. ξ) were obtained using an averaged Slater exponent for both the $5p_{1/2}$ and $5p_{3/2}$ AO's.

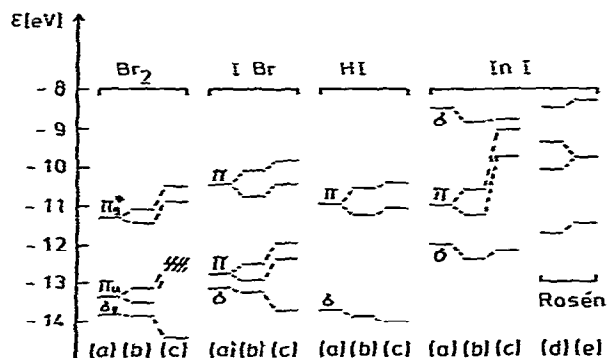


Fig. 2. Calculated non-relativistic (a), relativistic (b), DS DVM (d, ref. [21]), and HS DVM (e, ref. [21]) orbital energies together with experimental (c) orbital energies [16–18, 22] for Br_2 , IBr , HI , and InI .

by Wittel [5] and by Jungen [20]. We note that use of an averaged Slater exponent ζ for both the $5p_{1/2}$ and $5p_{3/2}$ AO's produces less satisfactory results than the use of different ζ 's. Fig. 2 shows results for Br_2 , IBr , HI , and InI , with the latter results compared to those obtained by Rosén [21] using the Dirac–Slater and Hartree–Slater discrete variational methods (DVM). Experimental orbital energies are also shown for Br_2 [16–18], HI [16], IBr [18] and InI [22]. The assumed bond lengths were 2.28, 1.61, 2.49, and 2.86 Å, respectively. Agreement with experiment is worse for IBr than for either Br_2 or I_2 (fig. 1), and is also somewhat unsatisfactory for InI , indicating the shortcomings of a non-charge-iterative method for molecules containing polar bonds.

Table 2 presents our calculated spin–orbit splittings of the valence-shell MO's of symmetry t_2 for the tetrahedral group IV hydrides. The splitting Δ is defined as positive when the u' (Γ_8 or $G_{3/2}$) level lies above the e'' (Γ_7 or $E_{5/2}$) level. These splittings are compared to the molecular Dirac–Fock one-center-expansion (DF OCE) [23,24] and atom Dirac–Fock np splittings [3]. We note that whereas the DF OCE splittings are similar to the corresponding DF central atom splittings, the REX splittings are significantly smaller. This is partly a result of our parameterization (table 1), which makes the high Z elements of this group very electropositive relative to hydrogen, so that an essentially hydridic description obtains, leading to a comparatively small spin–orbit splitting. Since the DF OCE method [23–28] does not in practice allow sufficient “delocalization” we anticipate that actual splittings should fall between the DF OCE and REX limits.

Fig. 3 presents a correlation diagram for the MO's of tetrahedral Bi_4 obtained using an assumed Bi–Bi distance of 3.0 Å. This species has been detected by mass spectrometry in the vapor in equilibrium with the liquid alloy BiSn [29], and is presumably similar to the more familiar species P_4 , As_4 , and Sb_4 . The highest occupied MO is the relativistic u' (Γ_8) or the non-relativistic a_1 MO, each at approximately -8 eV. The spin–orbit splitting of the t_2 levels at -8.94 and -14.43 eV are 1.07 and 0.05 eV, respectively, the former splitting being approximately one-half of the atomic $6p$ splitting of 2.11 eV (table 1), while the latter is nearly zero because of the predominant $6s$

Table 2
Spin–orbit splittings

Molecule	R^a (Å)	Δ (REX) (eV)	Δ (D–F) ^b (eV)	Δ (D–F, atom) ^c (eV)
CH_4	1.095	0.0045	0.01 0.0056 ^d	0.008
SiH_4	1.560	0.012	0.021 0.022 ^d	0.03
GeH_4	1.588	0.067	0.16	0.18
SnH_4	1.746	0.14	0.42	0.44
PbH_4	1.746	0.49	1.54	1.50
$(114)\text{H}_4$	1.746	1.68	5.16	4.66

^a) Distances chosen to match those used in refs. [23,24].

^b) Refs. [23,24]. ^c) Ref. [3].

^d) Includes non-spherical contributions.

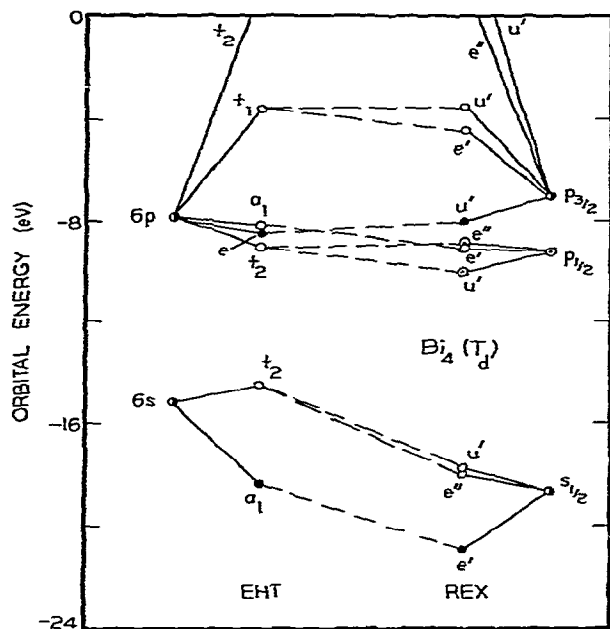


Fig. 3. Calculated non-relativistic (EHT) and relativistic (REX) orbital energy correlation diagram for Bi_4 with T_d symmetry and a Bi-Bi distance of 3.0 Å.

character of the lower energy t_2 MO. The ion Bi_4^{2-} would have two electrons in e' (Γ_6 or $E_{1/2}$) MO at -4.5 eV; although a closed-shell system, the gap to the vacant u' (Γ_8) MO is only 0.9 eV, so that a second-order Jahn-Teller instability is expected for tetrahedral Bi_4^{2-} (first-order in the non-relativistic description with two electrons in the t_1 MO). The ion Bi_4^{2-} is known in the solid state [30] as a planar species of D_{4h} symmetry with a Bi-Bi distance of 2.94 Å. Calculations (not shown) for a D_{4h} structure with a Bi-Bi distance of 3.0 Å suggest stability for the dianion, with the highest occupied MO being of e_g symmetry and lying 1.95 eV below a vacant b_{1u} symmetry MO (the designation with atoms lying between the x and y axes in the xy plane). This gap is reduced to 1.75 eV when relativistic parameters are used. Similar non-relativistic results were previously reported by Corbett [31].

The tetrahedral Bi_4 and the isoelectronic species Pb_4^{4-} are according to fig. 3 stabilized by the large $u'-e'$ distance. In Lauher's [32] terminology, our u' would be the highest "cluster valence molecular or-

bita" while the subsequent e' is the lowest "high lying anti-bonding orbital". As seen, this division is not essentially changed in the T_d case by relativistic effects.

4. Summary

Our basic philosophy concerning REX is that it provides a convenient and inexpensive procedure for "extrapolating" the results of Dirac-Fock atomic calculations to molecules, thus providing a semi-quantitative description of relativistic effects in chemical bonding. Comparisons are made between orbital energies and observed ionization energies. The experimental spin-orbit splittings of valence MO's are generally well reproduced by REX, while the absolute π -MO binding energies tend to be too large. Due to the absence of charge iteration, the hydrides of more electropositive metals tend to be too hydridic. Results for numerous other molecules will appear in a future publication [33].

References

- [1] R. Hoffmann, *J. Chem. Phys.* 39 (1963) 1397.
- [2] L.L. Lohr Jr. and W.N. Lipscomb, *J. Chem. Phys.* 38 (1963) 1607.
- [3] J.P. Desclaux, *At. Data Nucl. Data Tables* 12 (1973) 311.
- [4] R. Manne, K. Wittel and B.S. Mohanty, *Mol. Phys.* 29 (1975) 485.
- [5] K. Wittel, *Chem. Phys. Letters* 15 (1972) 555.
- [6] K. Wittel, B.S. Mohanty and R. Manne, *J. Electron Spectry. Related Phenomena* 5 (1974) 1115.
- [7] K. Wittel, H. Bock and R. Manne, *Tetrahedron* 30 (1974) 651.
- [8] K. Wittel and R. Manne, *Theoret. Chim. Acta* 33 (1974) 347.
- [9] K. Wittel and R. Manne, *J. Chem. Phys.* 63 (1975) 1322.
- [10] E.A. Boudreaux, T.P. Carsey, A. Dutta-Ahmed, E.S. Elder and L.E. Harris, *Abstracts of the EUCEM Conference on Electronic Structures of Transition Metal Complexes*, Maynooth, Ireland (1978).
- [11] I.B. Bersuker, S.S. Budnikov and B.A. Leizerov, *Intern. J. Quantum Chem.* 11 (1977) 543.
- [12] P. Pyykkö, *Advan. Quantum Chem.* 11 (1978) 353.
- [13] J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffmann, *QCPE* 10 (Suppl.) (1973) 344.
- [14] J. S. Griffith, *Theory of transition metal ions* (Cambridge Univ. Press, London, 1961).
- [15] M. Rotenberg, R. Bivins, N. Metropolis and J.K. Wooten Jr., *The 3-j and 6-j symbols* (The Technology Press, MIT, Cambridge, 1959) p. 4.

- [16] D.C. Frost, C.A. McDowell and D.A. Vroom, *J. Chem. Phys.* **46** (1967) 4255.
- [17] A.B. Cornford, D.C. Frost, C.A. McDowell, J.L. Ragle and I.A. Stenhouse, *J. Chem. Phys.* **54** (1971) 2651.
- [18] A.W. Potts and W.C. Price, *Trans. Faraday Soc.* **67** (1971) 1242.
- [19] C.Y. Yang, *Chem. Phys. Letters* **41** (1976) 588.
- [20] M. Jungen, *Theoret. Chim. Acta* **27** (1972) 33.
- [21] A. Rosén, *Intern. J. Quantum Chem.* **13** (1978) 509.
- [22] J. Berkowitz and J. L. Dehmer, *J. Chem. Phys.* **57** (1972) 3194.
- [23] J.P. Desclaux and P. Pyykkö, *Chem. Phys. Letters* **29** (1974) 534.
- [24] P. Pyykkö and J.P. Desclaux, *Nature* **226** (1977) 336.
- [25] J.P. Desclaux and P. Pyykkö, *Chem. Phys. Letters* **39** (1976) 300.
- [26] P. Pyykkö and J.P. Desclaux, *Chem. Phys. Letters* **42** (1976) 545.
- [27] P. Pyykkö and J.P. Desclaux, *Chem. Phys. Letters* **50** (1977) 503.
- [28] P. Pyykkö and J.P. Desclaux, *Chem. Phys.* **34** (1978) 261.
- [29] G. Riekert, P. Lamparter and S. Steeb, *Z. Naturforsch.* **31A** (1976) 711.
- [30] A. Cisar and J.D. Corbett, *Inorg. Chem.* **16** (1977) 2482.
- [31] J.D. Corbett, *Inorg. Nucl. Chem. Letters* **5** (1969) 81.
- [32] J.W. Lauher, *J. Am. Chem. Soc.* **100** (1978) 5305.
- [33] P. Pyykkö and L.L. Lohr Jr., to be published.