Empirically adjusted and consistent set of EHT valence orbital parameters for all elements of the periodic table

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Empirically adjusted and consistent set of EHT valence orbital parameters for all elements of the periodic table

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Abstract

The Hartree–Fock–Slater model of atoms has been modified by using individual values of the exchange parameter, α_{ex}, for each atom. Each value of α_{ex} was adjusted to reproduce the empirical value of the first ionization energy of the atom considered. The expectation values, energies and radial functions for all elements of the periodic table have been evaluated on the basis of the Hartree–Fock–Slater model and individual exchange parameters. A consistent set of Slater type orbital single ζ valence atomic orbital exponents and energies for all elements of the periodic table, suitable for orbital interaction analysis, is presented. These exponents were calculated by fitting the $\langle r \rangle_{STO}$ moments to numerical empirically adjusted $\langle r \rangle_{HFS}$ results. Qualitatively, the new parameters compare well with Fitzpatrick and Murphy exponents and Mann numerical Hartree–Fock $\langle r \rangle_{HF}$ moments and energy values but contain some influence of correlation and relativistic phenomena.

1. Introduction

In principle, we can perform pseudopotential DFT molecular orbital calculations on systems of almost any complexity. It is, however, often extremely profitable in terms of understanding the orbital structure to relate the level arrangement in a complex system to that of a simpler one. This kind of understanding can be reached through the orbital interaction approach [1, 2]. It is generally acknowledged that orbital interaction calculations are broadly divided into two categories. The first category focuses on providing a conceptual framework for considering the organization of experimental knowledge (understanding) [1, 2]. The second category generally relates to modelling a particular experimental property of a large system. An excellent new example of such a philosophy can be found in [3]. Although both categories are based on the molecular orbital concept, and an effective one-electron Hamiltonian, H^{eff}, they are notably

different in terms of semi-empirical definition of matrix representation, $H_{\mu\nu} = \langle \chi_\mu | H^{\text{eff}} | \chi_\nu \rangle$, on an atomic orbital basis. The choice of approach is generally a question of style and the interpretation desired.

In the first approach the diagonal element, $H_{\mu\mu}$, is estimated by the valence state ionization potential (VSIP) of the atomic orbital χ_μ and the off-diagonal element $H_{\mu\nu}$ is approximated as a function of the overlap integral $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$. In this approach, one should pay attention to the parameters of atomic orbitals used to construct the matrix elements since only functional dependence between $H_{\mu\nu}$ and $S_{\mu\nu}$ is the subject of a semi-empirical approximation. The firm foundation of such an orbital interaction philosophy was given by Hoffmann [4] in 1963 under the name extended Hückel (EH) theory. That approach used realistic atomic data (orbital energies and exponents) in orbital interaction calculations. It means that the method does not give all results accurately, but a universal parameter set can be used without suspicion that it is wrong for a particular purpose [5].

In constructing the matrix representation in the second approach, the problem of empirical parameters is treated more formally, sometimes avoiding any reference to their physical meaning. We suppose that some or all quantities such as $H_{\mu\mu}$, $H_{\mu\nu}$ and/or $S_{\mu\nu}$, that enter the EH method are assumed empirical parameters. Then their optimal values can be determined from the condition that the calculated molecular properties agree either with the corresponding experimental data or with the results of accurate calculations. Naturally, to ensure the generality of such parameters, we should select them for a series of distinct systems and for various physical properties. In the second approach, such a procedure has not so far been consistently employed on a large scale [6]. For that reason, the method is sometimes called the 'separated parameters for separate problems approach'.

The primary goal of this article is to generate an empirically adjusted and consistent set of valence orbital parameters for all elements of the periodic table, in the spirit of the first approach. One-electron radial wavefunctions and orbital energies can be obtained numerically by solution of the Hartree–Fock (HF) equations [7, 8]. However, for approximate comparative orbital interactions, calculations (the EHT formalism) where high accuracy is not required, simpler expressions for the radial wavefunctions are needed. Slater [9], long ago, recognized this need and proposed the use of an exponential function to describe the radial part of each atomic orbital (equation (1)).

$$R(r) = N r^{n^*-1} \exp(-\zeta r), \qquad \zeta = \frac{Z-s}{n^*}. \tag{1}$$

Values for n^* and rules for calculating the screening constant, s, were given. These functions (Slater orbitals) can be calculated for all elements of the periodic table but give poor approximations for $n^* = 3$ and upwards [10]. Subsequent workers retained the form of equation (1), sometimes as a linear combination, and used a variety of methods to obtain the optimum orbital exponent, ζ [11]. Such functions become known as Slater type orbitals (STOs). A limiting factor of existing parameter sets in orbital interaction analysis remains, in that they are not consistent and not accurate enough even in comparison with known experimental atomic properties. To overcome this, we suggest the use of the empirically adjusted Hartree–Fock–Slater (HFS) model of the atom [12] as the source of accurate data for estimation of one-electron energies and exponents. The relationship between the HF and the HFS description of atoms is well described in Herman and Skillman's original book [13]. The HFS model of the atom has been used for orbital exponent evaluations by Fitzpatrick and Murphy [14].

2. Evaluation of individual values of statistical exchange parameters α_{ex} for atoms

The HFS model of the atom entails self-consistent solution of (equations (2)–(5))

$$\left[\tfrac{1}{2}\nabla_1^2 + V_{\text{eff}}\right]\phi_i(1) = \varepsilon_i\phi_i(1), \tag{2}$$

where

$$V_{\text{eff}} = -\frac{Z}{r_1} + \int \frac{\rho(2)}{r_{12}}\,d\tau_2 - 3\alpha_{\text{ex}}\left(\frac{3}{8\pi}\right)^{1/3}\rho^{1/3} \tag{3}$$

and

$$\rho(1) = \sum_i n_i|\phi_i(1)|^2. \tag{4}$$

The ground-state energy is then determined from the equation

$$E[\rho] = \sum_i n_i\varepsilon_i - J[\rho] + K_{\text{ex}}[\rho]. \tag{5}$$

Our approach differs from the Fitzpatrick method in that the optimal exchange parameter, α_{ex}, was estimated for each atom in the periodic table. Originally, this idea was introduced by Slater and Johnson [15]. In section 4 of their paper, they have suggested a criterion for determining a value of the parameter α_{ex}. The suggested scheme was to determine the parameter α_{ex} in an atomic calculation and use the same values in molecular or solid-state calculations. Next Schwarz examined two criteria for determining the exchange parameter α_{ex} [16, 17]. These criteria are (i) adjustment of the statistical total energy to the HF total energy, leading to α_{HF}, and (ii) satisfaction of the virial theorem, leading to α_{vt}. Numerical calculations of Schwarz show that individual α_{HF} and α_{vt} values are almost the same [16, 17] and differ by not more than 0.001. But the HFS model of the atom used with α_{ex} values obtained according to procedure (i) or (ii) has the same disadvantage as the pure HF model [7, 8], correlation and relativistic phenomena are not included in such a model. It is consistent but not empirically adjusted. For empirical adjustment, we need an atomic property that is known for all atoms in the periodic table. According to the NIST Standard Reference Data Program [18], only the first ionization energy meets this constraint, except for astatine. In this work, for empirical adjustment, the individual value of the exchange parameter α_{ex} was fixed at a value that give an exact reproduction of the experimental first ionization energy of the atom considered according to Koopman's theorem. In that way, some correlation (very low individual α_{ex} value of the exchange parameter for Li) and relativistic phenomena (very high individual α_{ex} values for Pt, Au and Hg) are partially included [12] as shown in table 1.

In the following, we shall only give the relevant computational details for this particular case. The HFS calculations for atomic systems have been performed using the free-electron density approximation (FDA) program [19]. For comparison of the numerical results, the QCMP102 [20] package has been used. For evaluation of the individual exchange parameters of the elements, accurate ionization energy data have been used [18]. The original free electron-based universal α_{ex} parameter, introduced by Slater, equals $\tfrac{2}{3}$ and yields acceptable results, but sometimes other values are used [13, 14]. We have therefore modified the α_{ex} parameter individually for each atom to achieve equality of the calculated and experimentally observed first ionization energy. Results from the calculations for the whole periodic table are shown in table 1. The mean value of α_{ex} is 0.756, with a standard deviation 0.081, the lowest observed value, of lithium, is 0.540 and the highest, of gold, is 0.956.

Our goal is the construction of an empirically adjusted and consistent set of valence orbital parameters for all elements of the periodic table in the spirit of the first approach above. It may

Table 1. Empirically adjusted exchange parameters α (upper values), and corresponding virial ratio (lower values).

1 H 0.667* -2.000																		2 He 0.687 -1.937
3 Li 0.540 -1.924	4 Be 0.757 -1.915											5 B 0.784 -1.924	6 C 0.785 -1.932	7 N 0.791 -1.938	8 O 0.602 -1.958	9 F 0.647 -1.957	10 Ne 0.683 -1.956	
11 Na 0.627 -1.962	12 Mg 0.732 -1.958											13 Al 0.779 -1.959	14 Si 0.781 -1.961	15 P 0.785 -1.963	16 S 0.635 -1.972	17 Cl 0.665 -1.971	18 Ar 0.689 -1.972	
19 K 0.697 -1.972	20 Ca 0.739 -1.972	21 Sc 0.736 -1.973	22 Ti 0.718 -1.975	23 V 0.657 -1.978	24 Cr 0.828 -1.972	25 Mn 0.668 -1.978	26 Fe 0.691 -1.978	27 Co 0.654 -1.980	28 Ni 0.585 -1.982	29 Cu 0.775 -1.977	30 Zn 0.736 -1.979	31 Ga 0.777 -1.978	32 Ge 0.777 -1.978	33 As 0.773 -1.979	34 Se 0.644 -1.983	35 Br 0.665 -1.983	36 Kr 0.684 -1.983	
37 Rb 0.725 -1.982	38 Sr 0.742 -1.982	39 Y 0.735 -1.983	40 Zr 0.731 -1.983	41 Nb 0.869 -1.980	42 Mo 0.874 -1.980	43 Tc 0.693 -1.987	44 Ru 0.845 -1.982	45 Rh 0.832 -1.982	46 Pd 0.650 -1.986	47 Ag 0.804 -1.983	48 Cd 0.763 -1.984	49 In 0.780 -1.984	50 Sn 0.773 -1.985	51 Sb 0.744 -1.985	52 Te 0.660 -1.987	53 I 0.660 -1.988	54 Xe 0.673 -1.987	
55 Cs 0.764 -1.986	56 Ba 0.760 -1.986	57 La 0.745 -1.987	72 Hf 0.738 -1.989	73 Ta 0.782 -1.988	74 W 0.780 -1.988	75 Re 0.746 -1.989	76 Os 0.783 -1.988	77 Ir 0.812 -1.988	78 Pt 0.948 -1.986	79 Au 0.956 -1.986	80 Hg 0.884 -1.987	81 Tl 0.826 -1.988	82 Pb 0.797 -1.989	83 Bi 0.657 -1.991	84 Po 0.645 -1.991	85 At 0.667* -1.991	86 Rn 0.631 -1.992	
87 Fr 0.854 -1.989	88 Ra 0.808 -1.989	89 Ac 0.721 -1.991	104 Rf 0.690 -1.992															

58 Ce 0.729 -1.987	59 Pr 0.769 -1.987	60 Nd 0.768 -1.987	61 Pm 0.768 -1.987	62 Sm 0.769 -1.987	63 Eu 0.764 -1.987	64 Gd 0.763 -1.987	65 Tb 0.778 -1.987	66 Dy 0.781 -1.987	67 Ho 0.786 -1.987	68 Er 0.790 -1.987	69 Tm 0.794 -1.987	70 Yb 0.797 -1.987	71 Lu 0.640 -1.990
90 Th 0.827 -1.989	91 Pa 0.808 -1.990	92 U 0.840 -1.989	93 Np 0.843 -1.989	94 Pu 0.860 -1.989	95 Am 0.846 -1.989	96 Cm 0.786 -1.990	97 Bk 0.864 -1.989	98 Cf 0.869 -1.989	99 Es 0.881 -1.989	100 Fm 0.886 -1.989	101 Md 0.891 -1.989	102 No 0.895 -1.989	103 Lr 0.847 -1.990

* Value of free-electron gas scale factor.
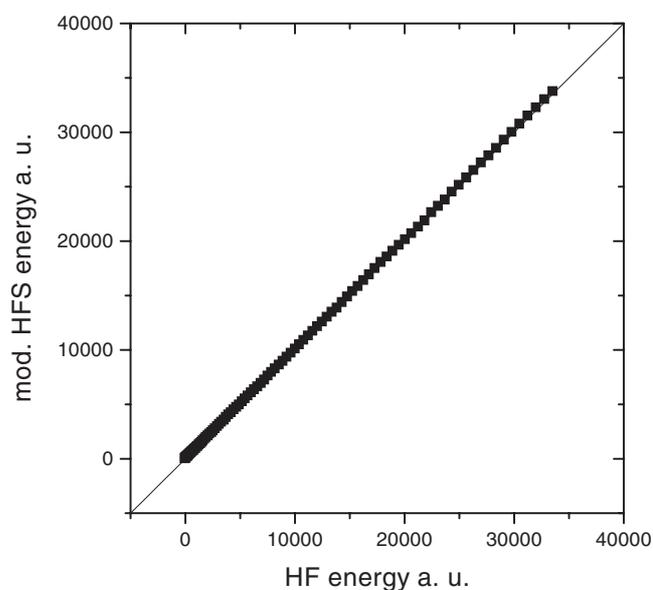
Figure 1. Correlation of modified HFS total binding energy with HF binding energy for all elements of the periodic table.
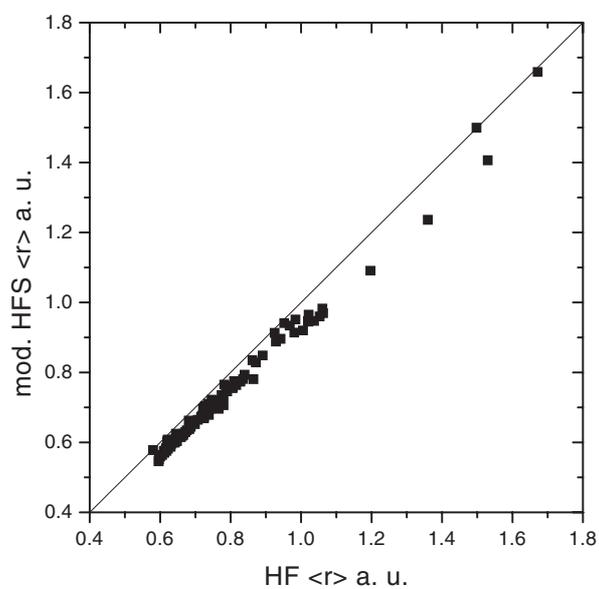
Figure 2. Correlation of modified HFS $\langle r \rangle$ expectation values with HF values for all elements of the periodic table.

be of particular importance to examine the computed properties of atoms in comparison with accurate HF results [7, 8]. The questions are how our total binding energy values compare with results of accurate HF calculations and what happen with radial expectation values when we introduce an individual set of α_{ex} parameters. Figure 1 shows the correlation between minus total atom energies and figure 2 the correlation between the $\langle r \rangle$ expectation values. The total

binding energy values calculated by our modified method are slightly larger (atoms are more stable) than HF values, and the modified HFS values are ~0.3% bigger than the HF values. The $\langle r \rangle$ expectation values calculated by our method are generally equal to or lower than HF values by about 6.2% (atoms are more compact). Both effects can be explained as being due to partial inclusion of electron correlation and relativistic phenomena by individual adjustment of α_{ex}. As seen in table 1, computed values of the virial ratio do not exactly equal -2. The difference shows a kind of price that we must pay for empirical parametrization of the HFS model. The results of basis set-free comparisons with HF results shows that our modified HFS model of atomic structure includes some correlation and relativistic phenomena. The modified HFS model can be treated as a source of atomic data for construction of an empirically adjusted and consistent set of valence orbital parameters for all elements of the periodic table.

3. Evaluation of empirically adjusted and consistent valence orbital parameter set for orbital interaction calculations

Routine applications of orbital interactions normally use perturbation molecular orbital theory, usually within the EHT formalism. These do not require extensive or highly accurate atomic wavefunctions. However, a consistent set within and between members of a series is most desirable. Typically, only a single exponent for the valence orbital is required, and each radial wavefunction can be represented by a single normalized STO (equation (6)).

$$R_k(r) = (2\zeta)^{k+1/2}((2k)!)^{-1/2}r^{k-1}\exp(-\zeta r). \tag{6}$$

Each numerical radial function obtained by HF or HFS theory displays oscillatory behaviour. For a given n and l the function has $n-l-1$ radial nodes, whereas a single STO has the property of being always positive. This difficulty can be overcome, and the single STO representation retained, by considering the equality of the radial expectation values for each atomic orbital (equation (7)).

$$\langle r \rangle_{STO} = \langle r \rangle_{HFS}. \tag{7}$$

Although the analytic STO cannot represent this inner behaviour adequately, the above approximation was considered desirable since the inner part of the radial function has an unimportant role in determining orbital interaction energy. Consequently, a basis set with an equal quality (single STO approximation) is more consistent. Optimal STO exponents ζ were determined using the iteration technique to solve equality (7). The *Mathematica* ® package was used to implement this procedure.

In all cases, the electronic configurations of the elements were those given by the NIST standard reference data program [18]. For some elements, virtual unoccupied orbitals are of interest [21]. Whenever such a situation occurred, exponents and orbital energies for both ground and excited states were computed.

Valence orbital energy values are given for the whole periodic table in table 2 and corresponding orbital exponents in table 3.

Qualitatively, the new parameters compare well with Fitzpatrick and Murphy's exponents [14] and Mann's calculated numerical HF $\langle r \rangle_{HF}$ moments and energy values [7, 8]. The differences are due to correlation and relativistic phenomena included by empirical estimation of the exchange parameters α_{ex} for each atom under consideration. According to the HFS model parametrization scheme, the energy of each HOMO orbital matches exactly the observed ionization energy of the atom considered. These new energy and exponent values are particularly useful for orbital interaction considerations according to the 'EH theory' idea introduced by Hoffmann [4]. To date, no complete consistent and empirically adjusted set is

Table 2. Energy of valence s-, p-, d- and f-orbitals of the elements (eV).

1 **H**																	2 **He**
1s -13.598																	1s -24.587

3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
2s -5.392	2s -9.323											2s -14.688	2s -20.337	2s -26.685	2s -28.541	2s -36.369	2s -44.924
2p -3.540	2p -5.600											2p -8.298	2p -11.260	2p -14.534	2p -13.618	2p -17.423	2p -21.565

11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
3s -5.139	3s -7.646											3s -11.839	3s -17.738	3s -19.803	3s -20.941	3s -25.452	3s -30.168
3p -3.091	3p -4.280											3p -5.986	3p -8.152	3p -10.487	3p -10.360	3p -12.968	3p -15.760

19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
4s -4.341	4s -6.113	4s -6.561	4s -6.828	4s -6.746	4s -6.766	4s -7.434	4s -7.902	4s -7.881	4s -7.640	4s -7.726	4s -9.394	4s -13.234	4s -16.579	4s -19.825	4s -20.658	4s -24.165	4s -27.781
4p -2.786	4p -3.744	4p -3.913	4p -3.973	4p -3.842	4p -3.739	4p -4.060	4p -4.228	4p -4.141	4p -3.956	4p -3.913	4p -4.664	4p -5.999	4p -7.899	4p -9.789	4p -9.752	4p -11.814	4p -14.000
		3d -9.450	3d -10.495	3d -10.370	3d -10.642	3d -13.017	3d -14.805	3d -14.821	3d -13.820	3d -14.100							

37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
5s -4.177	5s -5.695	5s -6.217	5s -6.634	5s -6.759	5s -7.092	5s -7.28	5s -7.360	5s -7.459	5s -6.441	5s -7.576	5s -8.994	5s -11.953	5s -14.519	5s -16.642	5s -17.703	5s -20.078	5s -22.737
5p -2.664	5p -3.703	5p -3.703	5p -3.866	5p -3.823	5p -3.951	5p -4.04	5p -3.983	5p -3.989	5p -3.352	5p -3.967	5p -4.686	5p -5.786	5p -7.344	5p -8.608	5p -9.010	5p -10.451	5p -12.130
		4d -7.173	4d -8.740	4d -10.261	4d -11.921	4d -12.59	4d -14.214	4d -15.333	4d -8.337	4d -17.401							

55 **Cs**	56 **Ba**	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
6s -3.894	6s -5.212	6s -5.577	6s -6.825	6s -7.550	6s -7.864	6s -7.833	6s -8.438	6s -8.967	6s -8.959	6s -9.225	6s -10.437	6s -12.402	6s -14.476	6s -14.658	6s -16.574	6s -19.9	6s -20.454
6p -2.544	6p -3.333	6p -3.480	6p -3.905	6p -4.264	6p -4.375	6p -4.288	6p -4.577	6p -4.830	6p -4.694	6p -4.786	6p -5.521	6p -6.108	6p -7.417	6p -7.286	6p -8.417	6p -10.7	6p -10.748
		5d -7.826	5d -8.419	5d -10.786	5d -12.293	5d -13.053	5d -15.450	5d -17.779	5d -19.695	5d -21.567							
		4f -10.702															

87 **Fr**	88 **Ra**	89 **Ac**	104 **Rf**
7s -4.073	7s -5.278	7s -5.17	7s -6.0
7p -2.637	7p -3.412	7p -2.25	7p -3.5
		6d -6.97	6d -8.1
		5f -7.93	

58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
6s -5.539	6s -5.473	6s -5.525	6s -5.582	6s -5.644	6s -5.670	6s -6.150	6s -5.864	6s -5.939	6s -6.021	6s -6.108	6s -6.184	6s -6.254	6s -5.426
6p -3.437	6p -3.450	6p -3.467	6p -3.488	6p -3.510	6p -3.507	6p -3.717	6p -3.603	6p -3.632	6p -3.668	6p -3.703	6p -3.739	6p -3.766	6p -3.369
5d -7.594	5d -4.944	5d -4.879	5d -4.813	5d -4.754	5d -4.615	5d -7.915	5d -4.617	5d -4.566	5d -4.520	5d -4.487	5d -4.441	5d -4.378	5d -5.428
4f -20.775	4f -16.405	4f -17.232	4f -18.010	4f -18.756	4f -19.164	4f -27.588	4f -20.900	4f -21.515	4f -22.133	4f -22.761	4f -23.305	4f -23.762	-

90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**
7s -6.307	7s -5.89	7s -6.194	7s -6.266	7s -6.026	7s -5.974	7s -5.991	7s -6.198	7s -6.282	7s -6.42	7s -6.50	7s -6.58	7s -6.65	7s -8.5
7p -3.918	7p -3.70	7p -3.883	7p -3.921	7p -3.837	7p -3.782	7p -3.692	7p -3.913	7p -3.956	7p -4.04	7p -4.08	7p -4.13	7p -4.16	7p -4.9
6d -9.951	6d -8.09	6d -9.115	6d -9.243	6d -6.324	6d -6.103	6d -8.430	6d -6.288	6d -6.315	6d -6.44	6d -6.46	6d -6.47	6d -6.46	6d -9.4
5f -16.685	5f -20.37	5f -23.373	5f -25.256	5f -22.862	5f -23.806	5f -27.871	5f -27.528	5f -29.215	5f -31.20	5f -32.87	5f -34.53	5f -36.13	-

Table 3. Single ζ Slater orbital exponents for valence s-, p-, d- and f-orbitals of the elements.

Z	Element	s	p	d	f
1	H	1s 1.0000	-	-	-
2	He	1s 1.6469	-	-	-
3	Li	2s 0.6534	2p 0.5305	-	-
4	Be	2s 1.0365	2p 0.8994	-	-
5	B	2s 1.3990	2p 1.2685	-	-
6	C	2s 1.7210	2p 1.6105	-	-
7	N	2s 2.0348	2p 1.9398	-	-
8	O	2s 2.2399	2p 2.0477	-	-
9	F	2s 2.5644	2p 2.4022	-	-
10	Ne	2s 2.8812	2p 2.7421	-	-
11	Na	3s 0.8675	3p 0.6148	-	-
12	Mg	3s 1.1935	3p 0.8809	-	-
13	Al	3s 1.5143	3p 1.1660	-	-
14	Si	3s 1.7580	3p 1.4337	-	-
15	P	3s 1.9860	3p 1.6755	-	-
16	S	3s 2.1362	3p 1.7721	-	-
17	Cl	3s 2.3617	3p 2.0176	-	-
18	Ar	3s 2.5796	3p 2.2501	-	-
19	K	4s 0.9362	4p 0.6914	-	-
20	Ca	4s 1.2112	4p 0.9329	-	-
21	Sc	4s 1.2870	4p 0.9828	3d 2.4341	-
22	Ti	4s 1.3416	4p 1.0104	3d 2.6439	-
23	V	4s 1.3570	4p 0.9947	3d 2.7809	-
24	Cr	4s 1.3804	4p 0.9784	3d 2.9775	-
25	Mn	4s 1.4761	4p 1.0641	3d 3.2208	-
26	Fe	4s 1.5465	4p 1.1114	3d 3.4537	-
27	Co	4s 1.5650	4p 1.1001	3d 3.6023	-
28	Ni	4s 1.5532	4p 1.0594	3d 3.7017	-
29	Cu	4s 1.5791	4p 1.0527	3d 3.8962	-
30	Zn	4s 1.7778	4p 1.2448	-	-
31	Ga	4s 2.0675	4p 1.5073	-	-
32	Ge	4s 2.2702	4p 1.7680	-	-
33	As	4s 2.4546	4p 1.9819	-	-
34	Se	4s 2.5680	4p 2.0548	-	-
35	Br	4s 2.7523	4p 2.2652	-	-
36	Kr	4s 2.9299	4p 2.4617	-	-
37	Rb	5s 1.0963	5p 0.7990	-	-
38	Sr	5s 1.3664	5p 1.0415	-	-
39	Y	5s 1.4613	5p 1.1100	4d 2.1576	-
40	Zr	5s 1.5393	5p 1.1647	4d 2.3831	-
41	Nb	5s 1.5926	5p 1.1738	4d 2.6256	-
42	Mo	5s 1.6579	5p 1.2186	4d 2.8241	-
43	Tc	5s 1.693	5p 1.249	4d 2.934	-
44	Ru	5s 1.7347	5p 1.2514	4d 3.1524	-
45	Rh	5s 1.7671	5p 1.2623	4d 3.3113	-
46	Pd	5s 1.6261	5p 1.1221	4d 3.0858	-
47	Ag	5s 1.8184	5p 1.2719	4d 3.6171	-
48	Cd	5s 1.9900	5p 1.4596	-	-
49	In	5s 2.4649	5p 1.6848	-	-
50	Sn	5s 2.4041	5p 1.9128	-	-
51	Sb	5s 2.5492	5p 2.0781	-	-
52	Te	5s 2.6576	5p 2.1718	-	-
53	I	5s 2.8080	5p 2.3390	-	-
54	Xe	5s 2.9595	5p 2.5074	-	-
55	Cs	6s 1.1993	6p 0.8918	-	-
56	Ba	6s 1.4519	6p 1.1397	-	-
57	La	6s 1.5331	6p 1.1979	5d 2.2743	4f 4.4161
72	Hf	6s 1.8411	6p 1.3822	5d 2.7702	-
73	Ta	6s 1.9554	6p 1.4857	5d 3.0193	-
74	W	6s 2.0190	6p 1.5296	5d 3.1936	-
75	Re	6s 2.0447	6p 1.5276	5d 3.3237	-
76	Os	6s 2.1361	6p 1.6102	5d 3.5241	-
77	Ir	6s 2.2167	6p 1.6814	5d 3.7077	-
78	Pt	6s 2.2646	6p 1.6759	5d 3.8996	-
79	Au	6s 2.3185	6p 1.7126	5d 4.0525	-
80	Hg	6s 2.4306	6p 1.8672	-	-
81	Tl	6s 2.5779	6p 1.9899	-	-
82	Pb	6s 2.7241	6p 2.1837	-	-
83	Bi	6s 2.7869	6p 2.2146	-	-
84	Po	6s 2.9312	6p 2.3830	-	-
85	At	6s 3.116	6p 2.62	-	-
86	Rn	6s 3.2053	6p 2.6866	-	-
87	Fr	7s 1.4160	7p 1.0598	-	-
88	Ra	7s 1.6336	7p 1.3011	-	-
89	Ac	7s 1.654	7p 1.289	6d 2.374	5f 3.796
104	Rf	7s 1.92	7p 1.45	6d 2.97	-
58	Ce	6s 1.5379	6p 1.1930	5d 2.2912	4f 4.9478
59	Pr	6s 1.5162	6p 1.1834	5d 2.0558	4f 4.8982
60	Nd	6s 1.5322	6p 1.1923	5d 2.0718	4f 5.0744
61	Pm	6s 1.5486	6p 1.2018	5d 2.0863	4f 5.2466
62	Sm	6s 1.5653	6p 1.2118	5d 2.0999	4f 5.4145
63	Eu	6s 1.5762	6p 1.2152	5d 2.0980	4f 5.5679
64	Gd	6s 1.6703	6p 1.2874	5d 2.4862	4f 5.9888
65	Tb	6s 1.6186	6p 1.2460	5d 2.1383	4f 5.9040
66	Dy	6s 1.6358	6p 1.2570	5d 2.1472	4f 6.0598
67	Ho	6s 1.6536	6p 1.2687	5d 2.1566	4f 6.2155
68	Er	6s 1.6723	6p 1.2813	5d 2.1668	4f 6.3703
69	Tm	6s 1.6898	6p 1.2928	5d 2.1731	4f 6.5208
70	Yb	6s 1.7063	6p 1.3030	5d 2.1754	4f 6.6686
71	Lu	6s 1.6647	6p 1.2167	5d 2.3795	-
90	Th	7s 1.8381	7p 1.4726	6d 2.6584	5f 4.3613
91	Pa	7s 1.777	7p 1.412	6d 2.571	5f 4.554
92	U	7s 1.8246	7p 1.4588	6d 2.6496	5f 4.7702
93	Np	7s 1.8451	7p 1.4739	6d 2.6940	5f 4.9412
94	Pu	7s 1.7983	7p 1.4366	6d 2.5123	5f 4.9882
95	Am	7s 1.8011	7p 1.4317	6d 2.5170	5f 5.1301
96	Cm	7s 1.8408	7p 1.4418	6d 2.7349	5f 5.3476
97	Bk	7s 1.8464	7p 1.4697	6d 2.5922	5f 5.4596
98	Cf	7s 1.8647	7p 1.4838	6d 2.6205	5f 5.6140
99	Es	7s 1.889	7p 1.505	6d 2.659	5f 5.774
100	Fm	7s 1.907	7p 1.519	6d 2.685	5f 5.922
101	Md	7s 1.924	7p 1.532	6d 2.709	5f 6.069
102	No	7s 1.940	7p 1.544	6d 2.730	5f 6.213
103	Lr	7s 2.13	7p 1.72	6d 2.99	-

available. Together with the universal force field (UFF) [22–24] as the geometry generator, the proposed parameter set premises that the vast majority of chemical phenomena may be qualitatively understood by judicious use of the very simple orbital interaction calculations. The software needed for such an approach is now readily available [25][1]. Generation of an approximate geometry and subsequent orbital interaction analysis is also possible using MM+ force field[2]. Good results have also been obtained using SYBYL force field as the geometry generator [26] and then transferring coordinates into YAeHMOP [27][3] through BabelWin [28]. Transferring through Babel is also possible into BICON-CEDIT [29], ICON-EDiT [30], CACAO [31] and CAESAR [32].

4. Choosing a Hückel constant k for an empirically adjusted and consistent valence orbital parameter set

The off-diagonal elements of EH theory, $H_{\mu\nu}$ ($\mu \neq \nu$), represent the effects of bonding between the atoms and are assumed to be proportional to the overlap, $H_{\mu\nu} \sim S_{\mu\nu}$. An approximation for differential overlap, referred to as the Mulliken approximation or generalized Mulliken approximation, can be used to estimate the off-diagonal elements, $H_{\mu\nu}$ [33] (equations (8)–(10))

$$H_{\mu\nu} = \frac{k' S_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu})}{2},$$ (8)

where

$$k' = k + \delta^2 + \delta^4(1 - k)$$ (9)

and

$$\delta = \frac{H_{\mu\mu} - H_{\nu\nu}}{H_{\mu\mu} + H_{\nu\nu}}.$$ (10)

The Hückel constant, k, has been inserted here as an adjustable parameter. It can be adjusted to give the best agreement with experiment. It is found that a good value is somewhat larger than would be indicated by the Mulliken approximation ($k = 1.0$). When one wishes to obtain a rough value of k for estimating orbital energies (or better, differences in orbital energies) in organic and organometallic compounds, hydrogen–hydrogen interactions are of great importance. According to Koopmans' theorem, the frontier orbital energies are given by (equation (11)).

$$-\varepsilon_{\text{HOMO}} = I,$$
$$-\varepsilon_{\text{LUMO}} = A.$$ (11)

Experimental values of the ionization potential, I, and electron affinity, A, of the H_2 molecule are $I = 15.4$ eV and $A = -2.0$ eV [34]. Using the experimental bond length of the H_2 molecule, 0.741 Å, the HOMO–LUMO gap, 17.4 eV, is reproduced with $k = 1.3681$. Note

[1] Program ArgusLab 3.0.0 is distributed by Planaria Software: (http://www.planaria-software.com). The file EHT.prm, containing the parameters described above for the ArgusLab 3.0.0 program can be obtained from the author on request (e-mail at holo@altis.chem.pg.gda.pl). Since memory for ArgusLab is dynamically allocated, the size of the calculation is limited only by the available system resources and the intrinsic limitations of the theories and algorithms employed. The largest system calculated on the author's PC (~200 MB) was a metallo-protein containing about 600 atoms. If you run calculations on bigger molecules, you will simply need more memory.

[2] Program HyperChem is distributed by Hypercube, Inc. (http://www.hyper.com). The file Exhuckel.abp, containing the parameters described above for the HyperChem program, can be obtained from the author on r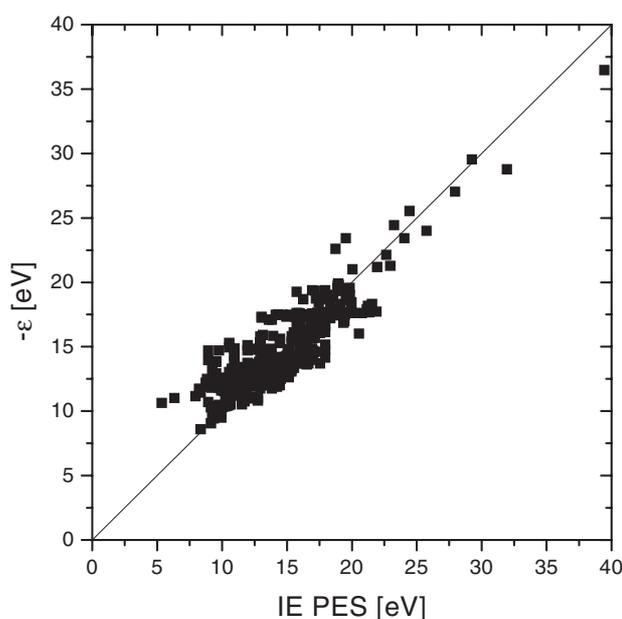equest (e-mail at holo@altis.chem.pg.gda.pl). The largest system calculated on the author's PC was the same as for ArgusLab.

[3] The eht_params.dat file containing the parameters described above for the YAeHMOP program can be obtained from the author on request (e-mail at holo@altis.chem.pg.gda.pl).

Figure 3. Correlation of EH eigenvalues, ε_n, with PES ionization energies of molecules. The *ab initio* STO-3G geometry and empirically adjusted and consistent parameter set of valence atomic orbitals were used as inputs for EH calculations. Experimental IE values in eV are after [35].

that the proportionality constant $k = 1.3681$ differs considerably from that introduced by Hoffmann [4] ($k = 1.75$) and used by many groups. However, in the common approach the hydrogen atom 1s orbital exponent is changed substantially from its original free atom value of $\zeta = 1.0$.

5. An example of an application relevant to the interpretation of photoelectron spectra

As an example of an application, the problem of predicting characteristic peaks in PES is considered. One hundred and six chemical compounds containing elements from hydrogen to uranium of known experimental PES data have been chosen [35]. The structures of compounds have been obtained by *ab initio* STO-3G energy minimization. Then EHT calculations were performed using the weighted Wolfsberg–Helmholz formula for $H_{\mu\nu}$ [33] and $k = 1.3681$. The principal use of PE spectroscopy is to determine the binding energies of the atomic and molecular orbitals. Ideally, when PE spectra are taken with a monochromatic photon source, one and only one PE peak will occur corresponding to each of the molecular orbitals since the binding energy is related to the PE energy. The binding energy of a given molecular orbital is the difference between the total energies of the initial and the final states, the initial state being the neutral molecule and the final state being the molecular ion in which an electron from the given orbital has been removed. Rather than using calculations of the total energies of the initial and final states in order to compare with experimental binding energies, the EH model employs eigenvalues calculated for the molecular orbitals of the neutral molecule on the basis of Koopmans' approximation. In the approximation, calculated eigenvalues ε_n are set equal to the binding energies of the frozen molecular orbitals. In this way, the eigenvalues are related

to the adiabatic binding energy by the expression (12)

$$-\varepsilon_n = E_{\text{bin}(n)} + E_{\text{R}}, \tag{12}$$

where E_{R} is the relaxation energy. In comparing experimental binding energies with theoretical calculations, it is most proper to use the onset of the vibrational envelope where $v' = 0$ since the adiabatic binding energy has a well-defined meaning. However, for spectra of more complex molecules it is often most practical to report the peak of the vibrational envelope, which is called the vertical ionization potential. The results of calculations are shown in figure 3 as the correlation between the $-\varepsilon_n$ and PES ionization energies for 745 occupied orbitals. The mean error value of $-\varepsilon_n$ is -0.38 eV, suggesting that no systematic error exist. The standard deviation of computed orbital energies is 1.58 eV and the maximal error is equal 5.65 eV for the $Fe(PF_3)_5$ molecule. The 'failures' found could be caused by the applied STO-3G geometry or the proposed parameter set, or they can originate from the EHT approximations [6].

6. Concluding remarks

Obviously the test presented above cannot be treated as an exhaustive one. However, it suggests that the valence orbital single-ζ exponents and orbital energies found perform well at least for the interpretation of PES data. Additional tests not reported in this work show that the proposed empirically adjusted and consisted set of valence orbital parameters is adequate for a qualitative structure–property correlation analysis comparable with the common traditional one popularized by Hoffmann. If one would like to obtain results compatible with the existing huge amount of literature data, then simply change the hydrogen atom orbital exponent to $\zeta = 1.3$ and Hückel constant to $k = 1.75$.

Acknowledgments

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