

## Inclusion of $3d$ Orbitals in Calculations Involving Second Row Atoms

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Valence-state ionisation potentials,  $I_\mu$ , and non-empirical one-centre electron repulsion integrals are evaluated for the separate  $3s$ ,  $3p$  and  $3d$  orbitals of Na, Mg, Al, Si, P, S, and Cl. These parameters are for use in the application of the CNDO SCMO method to molecules containing second row atoms.

Die Ionisierungspotentiale des Valenzzustands,  $I_\mu$  und die nicht-empirischen Ein-Zentren-Elektronen-Abstoßungsintegrale werden für die  $3s$ -,  $3p$ - und  $3d$ -Orbitale von Na, Mg, Al, Si, P, S und Cl angegeben. Diese Parameter werden bei der Anwendung der CNDO-SCMO-Methode auf Moleküle, die Atome der zweiten Reihe enthalten, benötigt.

On détermine les potentiels d'ionisation de l'état de valence  $I_\mu$  et les intégrales de répulsion monocentriques pour les orbitales  $3s$ ,  $3p$ ,  $3d$  de Na, Mg, Al, Si, P, S et Cl. Ces paramètres sont utilisés dans l'application de la méthode CNDO SCMO à des molécules contenant des atomes de la seconde colonne.

Much interest has been expressed in the effect of the empty  $3d$  orbitals on the chemistry of second-row atoms and CNDO SCMO calculations directed towards clarifying the problem are now being carried out [2, 8]. As part of a general investigation of the problems we have derived values for the basic input parameters needed for Pople-Segal-Santry type calculations on second row atoms using a basis set of  $3s$ ,  $3p$ , and  $3d$  orbitals. These parameters have been used by us in a series of calculations (to be reported fully later) on some organoaluminium and silicon compounds. They comprise both a) valence-state ionisation potential data for obtaining the diagonal core Hamiltonian matrix elements, and b) one-centre interelectronic repulsion integrals ( $\gamma_{\mu\mu}$ ). Some of the ionisation parameters have previously been derived semi-empirically although they were used in a rather different way [8, 9]. Our approach to the problem of the electron repulsion terms for CNDO all valence-electron calculations is however different to that employed by the previous workers (see later).

### Valence-State Ionisation Potentials

For the  $3s$  and  $3p$  electrons the  $I_\mu$  values are the valence-state ionisation potentials evaluated by the method of Hinze and Jaffé [3]. In computing these the valence-state promotion energies of the neutral atom and positive ion were

averaged over the energies of states making up the appropriate configuration [4] and weighted for multiplicity. The results are given in Table 1, and are in satisfactory agreement with those of Sichel and Whitehead [9].

Table 1. *Valence-state ionisation potentials*

Atom X	3s I.P. for X $I_s$ (eV)	3p I.P. for X $I_p$ (eV)
Na	5.14	3.04
Mg	7.64	4.52
Al	11.32	5.97
Si	15.15	7.62
P	19.37	10.84
S	20.52	10.78
Cl	25.29	13.99

When the same approach is applied to produce ionisation potentials for 3d electrons a conceptual difficulty is at once encountered, *i.e.* the 3d orbitals of neutral second row atoms are formally unoccupied. Even if this is ignored the incompleteness of spectroscopic data for *excited* configurations involving 3d electrons exacerbates the problem. The difficulty has been circumvented to some extent by extrapolation of the meagre data calculated for neutral elements [8] but we now present data which allows the valence-state ionization potentials for *d* orbitals to be obtained for a range of values of the orbital exponent  $Z^*$ . One limit corresponds to the supposition that an electron in a 3d orbital is, in effect, outside the whole neutral atom core (*i.e.* its energy will be related to the V.S.I.P. of the negative ion), whilst the other represents deep penetration into the core. This allows a high degree of flexibility in the 3d orbital form employed in a particular calculation and indeed this should be subjected to a variational-optimisation procedure.

Unfortunately, the ionisation potential of an electron in a 3d orbital of a second-row negative ion cannot be found directly from atomic spectroscopic data since only state energies for neutral and positively charged ions are available [4]. Hence we first calculated  $I_d$  for the uncharged and several charged species and extrapolated the values graphically to afford  $I_d$  for the negative ion. The energies of the spectroscopic states contributing to each configuration were averaged as before for the *s* and *p* configurations.

The states used and the resultant 3d ionisation potentials are shown in Table 2. Here  $Z^*$  is the effective nuclear charge calculated from Burn's rules.

The values of  $I_d$  for each species will depend to some extent upon which of its spectroscopic states have been observed; in the case of configurations involving 3d electrons, the spectroscopic data in the literature is in some cases incomplete. An attempt was made to correct for this in instances where most of the state-energies were available. For example,  $I_d$  for  $\text{Si}^0$  (Table 2) was obtained from the only two observed states,  $^3D$ ,  $^1D$ . If the corresponding pair of states alone is used to obtain  $I_d$  for  $\text{P}^+$ , then the result is 0.8% lower than that from the full range of states. The value of  $I_d$  for  $\text{Si}^0$  was therefore amended to 2.05 eV. This value is

shown in parentheses in Table 2. Similar corrections were applied to the 3d ionization potentials for  $S^{2+}$  and  $P^0$ , giving new values of 17.11 eV and 2.91 eV respectively.

For the  $3s^2 3p^3 3d$  configuration of  $S^0$ , only two out of the many possible spectroscopic states have been observed. Any correction of the above type would be too uncertain to be applied with confidence, and so  $I_d$  for  $S^0$  was disregarded and  $I_d$  for  $S^-$  was calculated solely from the data appertaining to the other negative

Table 2. Atomic states yielding  $I_d$  for second row elements

Atom or ion	Con-figuration	Atomic states	Ionized atom's or ion	Config-uration	Atomic states	$I_d$ (eV)	Effective nuclear charge $Z^*(X^{n+})$
$(X^{n+})$	$(X^{n+})$	$(X^{n+})$	$(X^{(n+1)+})$	$(X^{(n+1)+})$	$(X^{(n+1)+})$		
$Na^-$	$3s3d$		$Na^0$	$3s$		0.20	0.25
$Na^0$	$2p^6 3d$	$^2D$	$Na^+$	$2p^6$	$^1S$	1.52	1.00
$Na^+$	$2p^5 3d$	$^3P, ^3F, ^1F, ^1P, ^3D, ^1D$	$Na^{2+}$	$2p^5$	$^2P$	6.16	2.00
$Na^{2+}$	$2p^4 3d$	$^4D, ^4F, ^4P, ^2F, ^2D, ^2P, ^2G, ^2P, ^2D, ^2F, ^2S, ^2D$	$Na^{3+}$	$2p^4$	$^3P, ^1D, ^1S$	14.85	3.00
$Mg^-$	$3s^2 3d$		$Mg^0$	$3s^2$		0.35	0.50
$Mg^0$	$3s3d$	$^1D, ^3D$	$Mg^+$	$3s$	$^2S$	1.74	1.25
$Mg^+$	$2p^6 3d$	$^2D$	$Mg^{2+}$	$2p^6$	$^1S$	6.16	2.00
$Mg^{2+}$	$2p^5 3d$	$^3P, ^3F, ^1F, ^1P, ^1D, ^3D$	$Mg^{3+}$	$2p^5$	$^2P$	14.04	3.00
$Al^-$	$3s^2 3p3d$		$Al^0$	$3s^2 3p$		0.75	1.00
$Al^0$	$3s^2 3d$	$^2D$	$Al^+$	$3s^2$	$^1S$	1.96	1.50
$Al^+$	$3s3d$	$^3D, ^1D$	$Al^{2+}$	$3s$	$^2S$	6.52	2.25
$Al^{2+}$	$2p^6 3d$	$^2D$	$Al^{3+}$	$2p^6$	$^1S$	14.06	3.00
$Si^-$	$3s^2 3p^2 3d$		$Si^0$	$3s^2 3p^2$		1.10	1.50
$Si^0$	$3s^2 3p3d$	$^3D, ^1D$	$Si^+$	$3s^2 3p$	$^2P$	2.04	2.00
						(2.05)	
$Si^+$	$3s^2 3d$	$^2D$	$Si^{2+}$	$3s^2$	$^1S$	6.50	2.50
$Si^{2+}$	$3s3d$	$^1D, ^3D$	$Si^{3+}$	$3s$	$^2S$	16.39	3.25
$P^-$	$3s^2 3p^3 3d$		$P^0$	$3s^2 3p^3$		1.45	2.00
$P^0$	$3s^2 3p^2 3d$	$^2F, ^4D, ^4P, ^2P, ^2D$	$P^+$	$3s^2 3p^2$	$^3P, ^1D, ^1S$	2.86	2.50
						(2.91)	
$P^+$	$3s^2 3p3d$	$^3P, ^3D, ^1D, ^1P$	$P^{2+}$	$3s^2 3p$	$^2P$	6.66	3.00
$P^{2+}$	$3s^2 3d$	$^2D$	$P^{3+}$	$3s^2$	$^1S$	15.66	3.50
$S^-$	$3s^2 3p^4 3d$		$S^0$	$3s^2 3p^4$		1.80	2.50
$S^0$	$3s^2 3p^3 3d$	$^5D, ^3D$	$S^+$	$3s^3 3p^3$	$^4S, ^2D, ^2P$	3.06	3.00
$S^+$	$3s^2 3p^2 3d$	$^4D, ^4F, ^2F, ^4P, ^2P, ^2D$	$S^{2+}$	$3s^2 3p^2$	$^3P, ^1D, ^1S$	10.16	3.50
$S^{2+}$	$3s^2 3p3d$	$^3P, ^3D$	$S^{3+}$	$3s^2 3p$	$^2P$	16.97	4.00
						(17.11)	
$Cl^-$	$3s^2 3p^5 3d$		$Cl^0$	$3s^2 3p^5$		2.20	3.00
$Cl^0$	$3s^2 3p^4 3d$	no states obs.					
$Cl^+$	$3s^2 3p^3 3d$	$^5D, ^3D, ^1D, ^1F, ^3F, ^1P, ^3G, ^1P, ^1D, ^3D, ^3F, ^3P, ^3D, ^3S, ^3P$	$Cl^{2+}$	$3s^2 3p^3$	$^4S, ^2D, ^2P$	8.54	4.00
$Cl^{2+}$	$3s^2 3p^2 3d$	$^4F, ^4D, ^4P, ^2D, ^2P, ^2D, ^2F, ^2P$	$Cl^{3+}$	$3s^2 3p^2$	$^3P, ^1D, ^1S$	19.46	4.50

ions of the series (see below). Similarly, no series was plotted for the ions of chlorine since no levels appear to have been observed for  $\text{Cl}^0$  ( $3s^2 3p^4 3d$ ).

The values of  $I_d$  (corrected where necessary) for  $\text{X}^{n+}$  were plotted against  $Z^*$  for each of the elements Na, Mg, Al, Si and P (Fig. 1). All the curves are smooth and pass through the origin since the ionization potential must be zero when there is no effective nuclear charge. From each curve, the extrapolated value of  $I_d$  at the appropriate  $Z^*$  for the negative ion was abstracted and these figures were replotted against  $Z^*$ . The points fall on a good straight line,  $I_d = 0.733 Z^*$  and the relevant figures for  $\text{S}^-$  and  $\text{Cl}^-$ , hitherto inaccessible, were read off.

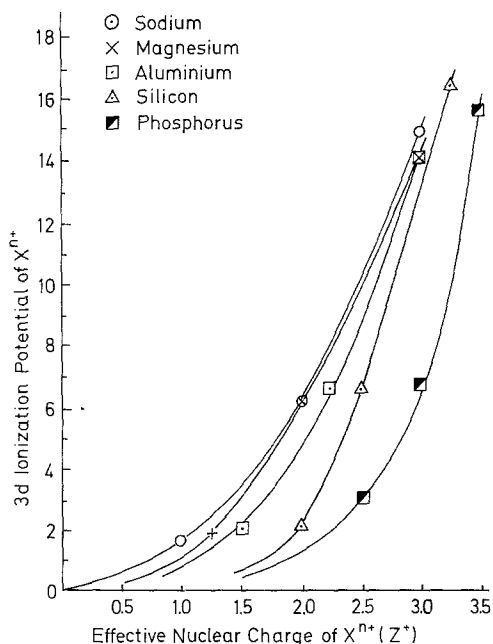


Fig. 1. 3d valence-state ionisation potential vs.  $Z^*$  for second row atoms

The  $d$  ionization potentials for the negative ions of all the second row elements are also listed in Table 2.

Although Table 2 gives explicitly only the  $d$  ionisation potential for specific oxidation states, nevertheless the curves of Fig. 1 may be used to derive appropriate  $I_d$  values for any intermediate case *i.e.* when the orbital exponent is varied in the inclusion of  $d$  orbitals.

### One-Centre Electron Repulsion Integrals

Previous calculations have adhered solely to purely theoretical  $s$ -type orbital forms in computing the one and two- centre electron repulsion integrals [7, 8]. All the one-centre interaction integrals are thus assigned values characteristic of the atom concerned. By doing this the invariance of the total energy to similarity transformations is preserved. It is, however, desirable to use, if possible, the

individual  $s$ ,  $p$  and  $d$  functions in computing these integrals. This is because,  $\gamma_{ss}$ , and  $\gamma_{pp}$  while not usually differing from each other by more than 2–3 eV, could be considerably greater than  $\gamma_{dd}$ . The same reasoning applies to the cross terms  $\gamma_{sp}$ ,  $\gamma_{pp'}$ ,  $\gamma_{sd}$ , and  $\gamma_{pd}$ .

We have therefore calculated the one-centre  $2s2s$ ,  $3s3s$ ,  $2p2p$ ,  $3p3p$ , and  $3d3d$  repulsion integrals for the atoms H, Li to Ne, and Na to Cl purely theoretically by employing Burn's functions and expanding the operator  $1/r_{ij}$  in the Neumann series of spherical harmonics

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_l^m(\theta_i, \phi_i) Y_l^{m*}(\theta_j, \phi_j)$$

and evaluating the series of improper integrals (the number of these is limited by symmetry).

Table 3. *One-centre repulsion integrals (eV)*

Atom	1s 1s				
H	20.404				
Atom	2s 2s	2p 2p			
Li	6.039	5.422			
Be	9.059	8.134			
B	12.330	10.845			
C	15.601	14.369			
N	18.873	17.894			
O	22.144	21.418			
F	25.415	24.943			
Ne	28.686	28.467			
Atom	3s 3s	3p 3p	$3d\ 3d(M^-)$ $3s^* 3p^m 3d$	$3d\ 3d(M^0)$ $3s^n 3p^{m-1} 3d$	$3d\ 3d(M^0)$ $3s^{n-1} 3p^m 3d$
Na	6.321	4.062	0.627	—	2.508
Mg	7.726	5.331	1.254	—	3.135
Al	9.247	6.601	2.508	3.762	4.389
Si	10.769	8.251	3.762	5.016	5.643
P	12.291	9.901	5.016	6.269	6.896
S	13.812	11.551	6.269	7.523	8.150
Cl	15.334	13.202	7.523	8.777	9.404

The data are given in Table 3. In the case of the  $d$  orbitals the Burn's exponents appropriate to both the neutral atom and the negative ion have been incorporated. In the elements aluminium to chlorine inclusive, the electron repulsion integrals for both the configurations  $3s^2 3p^{n-1} 3d$  and  $3s 3p^n 3d$  have been included. These configurations are distinguished by Burn's but not by Slaters screening rules.

We further suggest that both the 'atomic' terms ( $\gamma_{sp}$ ,  $\gamma_{sd}$ ,  $\gamma_{pp'}$ ,  $\gamma_{dd'}$ ) and the genuine two-centre repulsion integrals (both off-diagonal in the electron repulsion matrix) be obtained from the one-centre values by using either the Mataga [5]

or the Ohno [6] approximations. Test calculations were carried out on the sodium chloride molecule using different *s*, *p*, *d* basis sets and the three types of integrals (this work will be described more fully at a later date). The change of total energy with different bases was found to be negligible in this case.

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