Graphite intercalation compounds: exchange parameters and self-consistent analytical potentials

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Abstract. We determine the exchange parameter α which occurs in the X_α local statistical exchange approximation. An $\alpha = \alpha(Z)$ law is proposed. The effective charges for the different atomic numbers are compared with the values obtained by Slater and by Clementi and Raimondi. Transition Slater state energies are tabulated.

Crystal exchange parameters are proposed for graphite intercalation compounds.

1. Introduction: the binary compounds of graphite [1]

First, we recall information on a series of the first-stage intercalation compounds of graphite with alkali metals M. The different graphite intercalation compounds (GICs) are MC_6 or MC_8 (M ≡ Li, Ba, Sm, Sr, Ca, Eu, Yb for MC_6 and M ≡ Cs, Rb, K for MC_8).

Graphite (figure 1) is composed of graphitic sheets called 'graphene' for which the
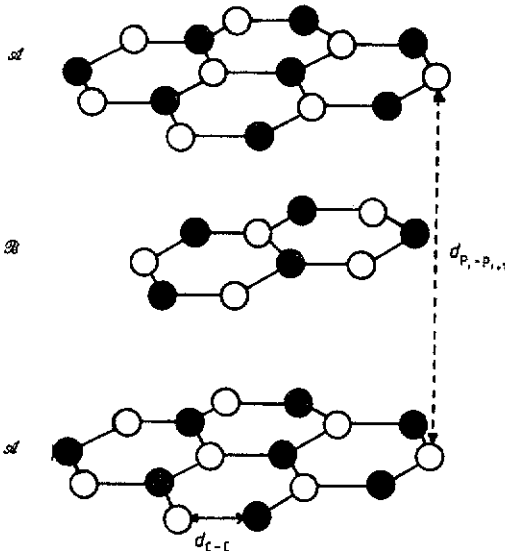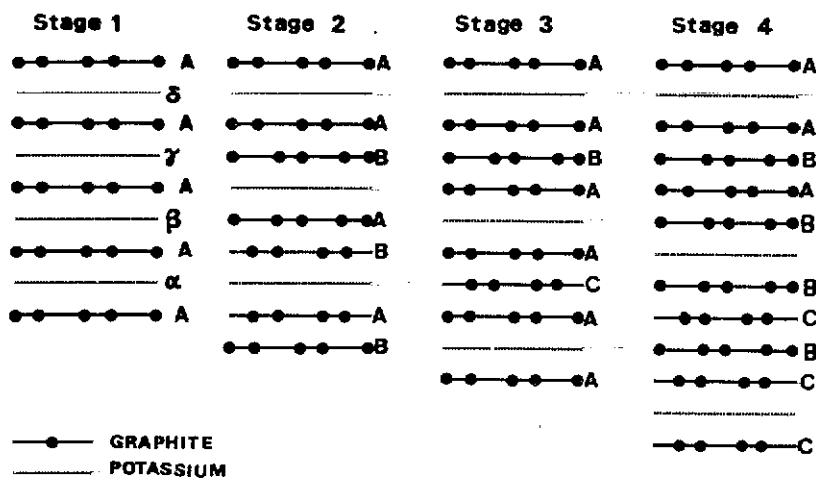

Figure 1. Graphitic planes.

Figure 2. Stacking phenomenon.

gap is zero. This confers to it an amphoteric character with zero-energy requirements either for donating electrons to electron acceptors such as halogens (Fe, Cl_2, Br_2 and I_2) or for abstracting electrons from alkali-metal atoms (Li, Na, K, Rb, Cs, etc).

GTCs are also classified by a stage n denoting the number of graphite layers between adjacent intercalate layers as is illustrated in figure 2 for potassium graphite.

After insertion, for the binary compound of graphite, the stacking of graphitic planes has changed from $\mathcal{A}$ $\mathcal{B}$ $\mathcal{A}$ $\mathcal{B}$ $\mathcal{A}$ to $\mathcal{A}$ $\mathcal{A}$ $\mathcal{A}$ $\mathcal{A}$ $\mathcal{A}$ (figure 1); the carbon atoms of the closest graphitic planes superpose exactly one above the other (this is not the case for pure graphite or the parent material).

The inserted atoms, located between the graphitic planes, will be referred to by Greek letters α, β, γ and δ according to the binary compounds studied. Figure 3 shows the α, β, γ and δ sites in the case of KC_8 compounds for the first stage.

For each compound, Hérold [2] and collaborators have shown (table 1) that the carbon–carbon distance in the same plane $\mathcal{P}$, and the distance between two neighbouring
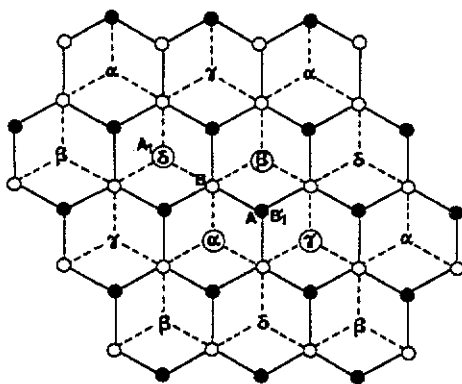

Figure 3. Notation α, β, γ, δ.

Table 1. Binary compounds

Compound	Symmetry	d_{C-C}	$d_{p_{i+1}-p_i}$
Graphite	$\mathcal{A}\mathcal{B}\mathcal{A}\mathcal{B}$	1.419	3.348
LiC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha$	1.433	3.706
CaC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.439	4.60
SrC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.437	4.94
BaC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.434	5.255
SmC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.449	4.58
EuC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.437	4.871
YbC$_6$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$	1.440	4.573
KC$_8$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\delta$	1.432	5.35
RbC$_8$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\delta$	1.431	5.65
CsC$_8$	$\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\alpha$	1.430	5.92

graphite planes change. According to the compounds studied, we see (figures 4–7) that the stackings of the inserted atoms are different.

We have four types of structure for the series studied: a stacking $\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha$ for the Li compounds, a stacking $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$ for the Ca, Sr, Sm, Ba, Eu and Yb compounds, a stacking $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\alpha$ for the Cs compounds and at least a stacking $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\delta$ for the Rb and K compounds.
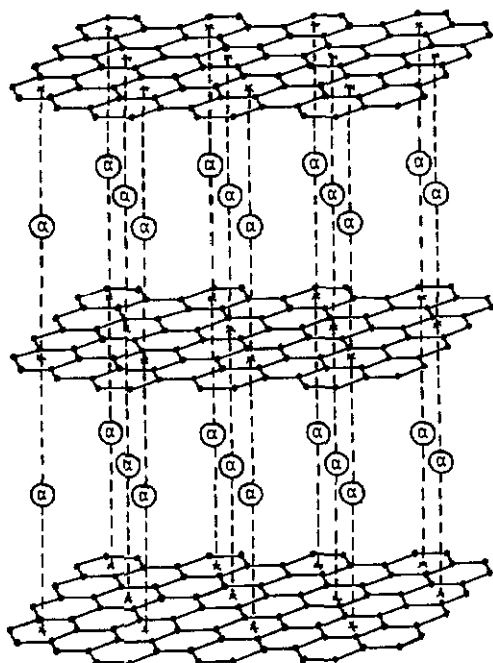
Figure 4. Type $\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha\mathcal{A}_\alpha$.
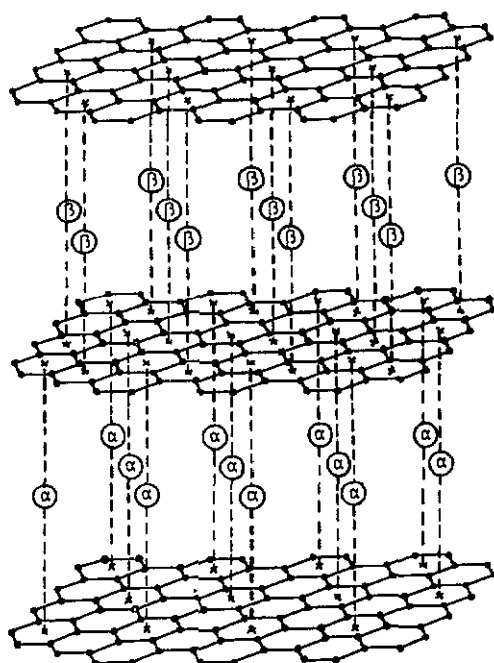
Figure 5. Type $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\alpha\mathcal{A}_\beta$.
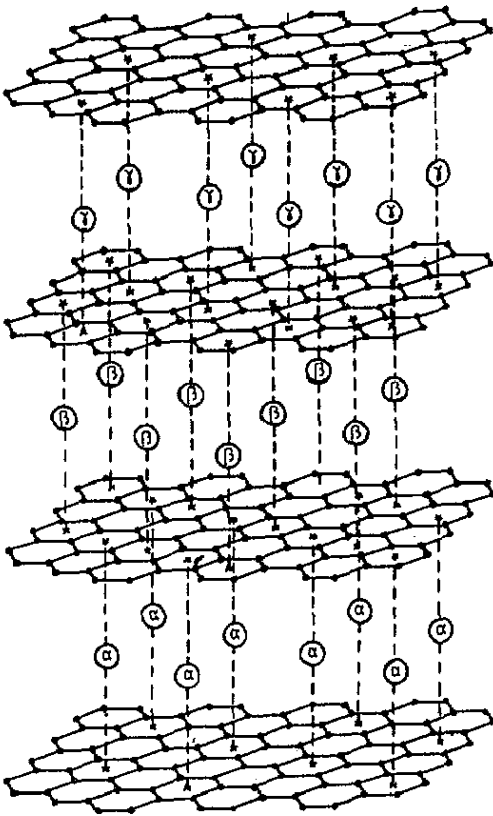
Figure 6. Type $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_\alpha$.
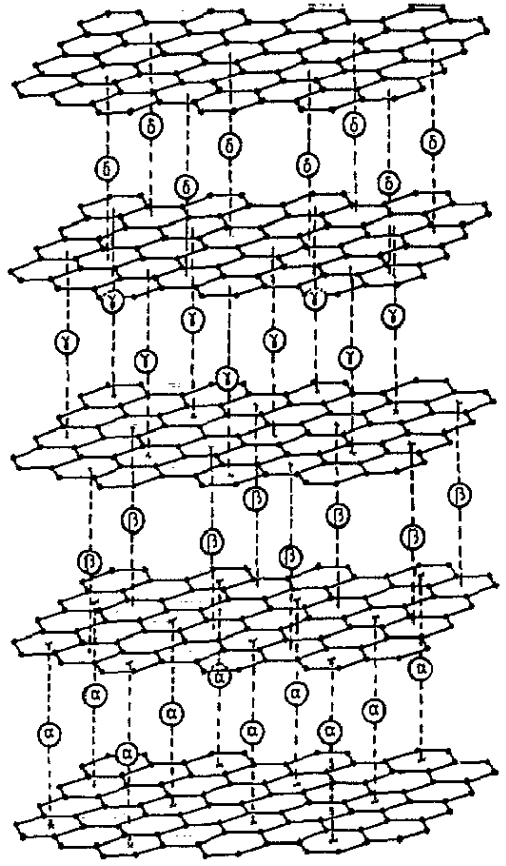
Figure 7. Type $\mathcal{A}_\alpha\mathcal{A}_\beta\mathcal{A}_\gamma\mathcal{A}_b$.

2. De Launay method

The de Launay [3] method [4] enables one to construct a potential $W(r)$ applicable to lattice dynamics calculus:

$$W(r) = W^{\text{at}}(r) + W^{\text{two-body}}(r) \tag{1}$$

where

$$W^{\text{at}}(r) = W^{\text{at}}_{\text{Coulomb}}(r) + \alpha W^{\text{at}}_{\text{exchange}}(r) \tag{2}$$

is the self-consistent Hartree–Fock atomic potential and

$$W^{\text{two-body}}(r) = A_1(r - r_a)^2 \exp(-r/\rho) + A_2(r - r_c)^2 \exp(-r/\rho) \tag{3}$$

is a two-body potential ('modified Born–Mayer [5] potential').

The atomic force constants α_1, α_2, α_3, α'_1 and α'_3 are related to the first and second derivatives of potential W:

$$\alpha_i = (\partial^2 W/\partial r^2)_{r=r_i} \tag{4}$$

$$\alpha'_i = (1/r)(\partial W/\partial r)_{r=r_i}. \tag{5}$$

The phonon dispersion curves for graphite, particularly the vibration frequencies at the Γ point (the centre of the Brillouin zone), are used to determine the values of α_i and α_i'.

The five coefficients r_a, r_c, A_1, A_2 and ρ appearing in (3), are fitted in a way that the analytical expression (1) gives the 'experimental' values of α_i and α_i' when we consider equations (4) and (5).

If one uses for the atomic potential the values α_{vt} published by Schwarz [6], the stability parameters r_a and r_c differ from the in-plane carbon–carbon distance d_{C-C} in graphite and from $d_{p_i-p_{i+1}}$, the distance between two successive graphitic planes (cf table 2); a better correlation is obtained for our α-value.

3. The α statistical exchange parameter [8–25]

When one uses the self-consistent Hartree–Fock method for obtaining wavefunctions and potentials, an exchange term is introduced. This negative term improves the stability.

The X_α method ordinarily used [26] is a statistical approximation and is well established. Schwarz [6] gave a table of α-values satisfying the virial theorem.

Another possibility is given by the 'local-density approximation' to the density functional method which approximates exchange and correlation. Least-square fits to potentials and wavefunctions can be made for 'local-density approximations [27].

We use an equivalent method of determining the α-parameter of the X_α Slater theory. This method determines for a given atom (or Z-value) and for a given value of α the X_α potential $W^{at}(r)$ using Hartree–Fock self-consistent wavefunctions.

Then, we obtain a polynomial approximate expression for $rW^{at}(r)$ by performing a best fit. Finally we require that this polynomial has the first term equal to $-Z$ and we determine α from such a condition [28].

4. Optimal value of the exchange parameter

The technique used is derived from the method of Lafon and Lin [29]. The resolution of single-electron Hartree–Fock equations, is performed by means of a FORTRAN program [30].

The computed potentials are obtained as a function of the distance r in the form of a table of 251 values (the distance scale is logarithmic).

Table 2. Stability parameters.

	d_{C-C} (Å)	$d_{p_i-p_{i+1}}$ (Å)
Gupta [7]	1.33	3.18
$\alpha_{Schwarz}$ [6]	1.35	3.32
$\alpha_{our\ value}$	1.417	3.339
Graphite	1.419	3.349

Table 3. Coefficients a_n.

Atomic coefficients	H	He	Li	Be	B	C	N	O	F	Ne
a_0	-1.000 000 0	-1.999 999 8	-2.999 999 9	-3.999 999 8	-4.999 999 5	-5.999 999 9	-6.999 999 8	-7.999 999 9	-8.999 999 9	-9.999 999 5
a_1	0.0	1.638 142 3	3.537 246 5	4.845 350 6	6.983 814 0	9.508 617 4	12.397 442	15.611 865	19.188 108	23.126 130
a_2	0.0	-0.866 090 8	-2.316 958 3	-3.498 282 2	-6.125 807 7	-9.580 042 6	-13.915 448	-19.020 931	-25.084 870	-32.169 038
a_3	0.0	0.207 426 5	0.739 865 9	1.368 497 9	3.074 903 4	5.736 780 4	9.572 951 0	14.515 100	20.884 537	28.852 347
a_4	0.0	-0.025 697 5	-0.126 869 6	-0.302 221 2	-0.879 647 5	-1.981 120 3	-3.850 133 5	-6.575 927 9	-10.476 124	-15.810 071
a_5	0.0	0.001 686 4	0.011 890 5	0.037 299 5	0.139 924 5	0.380 872 8	0.865 250 6	1.676 675 8	2.980 251 0	4.952 235 7
a_6	0.0	-0.000 056 1	-0.000 572 1	-0.002 386 2	-0.011 456 3	-0.037 639 4	-0.099 999 3	-0.220 551 4	-0.438 957 8	-0.806 241 5
a_7	0.0	0.000 000 74	0.000 011 0	0.000 061 3	0.000 375 0	0.001 484 9	0.004 612 0	0.011 594 9	0.025 885 1	0.052 653 6

Table 4. Exchange parameters.

Atom	α	$\alpha_{Schwarz}$	Atom	α	$\alpha_{Schwarz}$	Atom	α	$\alpha_{Schwarz}$
H	0.992 10	0.978 04	Ca	0.697 90	0.719 41	Y	0.653 86	0.704 40
He	0.974 40	0.772 36	Sc	0.693 67	0.717 93	Zr	0.653 28	0.703 98
Li	0.750 57	0.780 87	Ti	0.690 16	0.716 48	Nb	0.653 18	0.703 57
Be	0.903 22	0.767 56	V	0.687 08	0.715 06	Mo	0.653 44	
B	0.885 31	0.764 52	Cr	0.683 87	0.712 96	Tc	0.654 02	
C	0.864 99	0.758 47	Mn	0.681 78	0.712 28	Ru	0.655 05	
N	0.846 14	0.751 18	Fe	0.679 48	0.710 94	Rh	0.656 33	
O	0.832 38	0.743 67	Co	0.677 09	0.709 66	Pd	0.657 29	
F	0.817 22	0.736 51	Ni	0.675 54	0.708 43	Ag	0.659 56	
Ne	0.800 76	0.729 97	Cu	0.666 84	0.706 35	Cd	0.661 33	
Na	0.804 29	0.730 44	Zn	0.664 96	0.706 19	In	0.663 03	
Mg	0.784 56	0.728 50	Ga	0.670 33	0.706 44	Sn	0.664 67	
Al	0.766 90	0.727 95	Ge	0.667 99	0.706 45	Sb	0.666 20	
Si	0.750 29	0.726 96	As	0.665 62	0.706 30	Te	0.667 60	
P	0.737 52	0.725 69	Se	0.663 17	0.706 06	I	0.668 87	
S	0.727 38	0.724 26	Br	0.660 75	0.705 76	Xe	0.669 98	
Cl	0.718 84	0.722 77	Kr	0.658 42	0.705 44	Cs	0.672 20	
Ar	0.711 10	0.721 31	Rb	0.656 39	0.705 25	Ba	0.671 09	
K	0.704 07	0.720 72	Sr	0.654 90	0.704 80			

A least-squares fitting transforms these results into a polynomial

$$rW^{at}(r) = \sum_{n=0}^{N} a_n r^n. \tag{6}$$

A value of $N = 7$ is sufficiently satisfactory to obtain a good χ^2 criterion [31] (precision of around 10^{-5} Hartree).

In order to fulfil the preceding condition, α is varied until the coefficient a_0 is identical with the $-Z$-value (table 3). This leads to table 4 which provides exchange parameters α for different atoms.
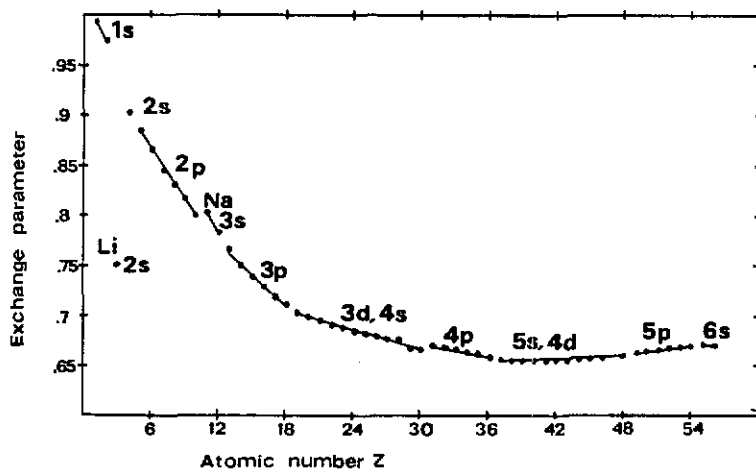

Figure 8. Exchange parameters as a function of Z.

Table 5. Physical properties of alkali metals.

	Li	Na	K	Rb	Cs	Mg
r_{atom} (nm)	0.123	0.157	0.203	0.216	0.235	0.136
r_{ionic} (nm)	0.068	0.097	0.133	0.147	0.167	0.066
T_{fusion} (°C)	180.54	97.83	63.65	39.00	28.45	651
$T_{water\,vapour}$ (°C) (760 mm Hg)	1330	881.3	757	696	670	1107

The equality (6) must validate the virial theorem and verify the following condition when we are very close to the nucleus [32] (i.e. $r \rightarrow 0$):

$$\lim_{r \to 0} \left[rW^{at}(r) \right] = -Z. \tag{7a}$$

This last condition is not verified when the values of the statistical exchange parameter α take for respective values those determined by Slater or by Schwarz [6].

The coefficients a_0 satisfying the virial theorem and associated with different polynomials representing the atomic potential of carbon atom are $-6.007\,320\,4$, inferior to -6 for $\alpha_{Slater} = 1$ and $-5.995\,667\,0$, superior to -6 for $\alpha_{Schwarz} = 0.758\,47$.

The new statistical exchange parameters α satisfying

$$\lim_{r \to 0} \left[rW^{at}(r) \right] = -a_0 \tag{7b}$$

are represented in figure 8 as a function of atomic number Z of different atoms considered. They are classified according to atomic levels. Except for the lithium atom, α varies with the atomic number Z. This can be explained by the common (physical and chemical) properties of magnesium and lithium atoms [33]. The atomic and ionic radii

Table 6. Transition-state energies.

Atom	1s	2s	2p	3s	3p
H	−0.500 000 0				
He	−0.849 486 1				
Li	−1.913 696 1	−0.195 499 8			
Be	−4.208 560 2	−0.285 114 5			
B	−6.983 910 6	−0.432 452 9	−0.223 989 2		
C	−10.407 454	−0.598 688 8	−0.294 954 6		
N	−14.496 987	−0.782 400 2	−0.369 889 0		
O	−19.268 473	−0.985 953 2	−0.449 876 9		
F	−24.709 796	−1.207 192 0	−0.532 933 1		
Ne	−30 821 524	−1.445 898 3	−0.618 674 0		
Na	−38.227 508	−2.158 486 7	−1.146 203 5	−0.182 279 3	
Mg	−46.493 087	−3.033 172 8	−1.841 130 9	−0.226 072 3	
Al	−55.653 294	−4.066 963 4	−2.691 839 6	−0.324 344 5	−0.153 417 7
Si	−65.645 354	−5.203 984 4	−3.641 892.0	−0.434 369 8	−0.197 316 2
P	−76.489 602	−6.452 646 0	−4.699 669 2	−0.547 636 5	−0.246 548 4
S	−88.187 355	−7.816 865 1	−5.869 224 5	−0.664 893 9	−0.299 607 3
Cl	−100.736 99	−9.298 030 6	−7.152 015 8	−0.786 847 1	−0.356 107 9
Ar	−114.135 69	−10.896 349	−8.548 268 1	−0.913 771 9	−0.415 802 1
K	−128.653 34	−12.876 787	−10.323 730	−1.273 395 3	−0.684 669 4

for these two atoms are very close (table 5). To sum up, it does not seem surprising that the exchange parameter value α for lithium is close to the value for magnesium.

The exchange parameter α as a function of Z is replaced by the expression $\alpha(Z)$ for Z-values between 1 and 56 inclusive:

$$\alpha(Z) = 1.022\,733\,8 - 3.134\,406\,3 \times 10^{-2}\,Z + 1.079\,068\,9\,10^{-3}\,Z^2$$
$$- 1.805\,773\,6\,10^{-5}\,Z^3 + 1.272\,331\,7\,10^{-7}\,Z^4 - 9.197\,432\,2\,10^{-11}\,Z^5. \tag{8}$$

This relation has no physical meaning but is interesting for systematic evaluations.

The energies associated with the different electrons of these atoms are slightly different from those given by Herman and Skillman (34). This is normal; the orbital energies reported in table 6 should not be interpreted as ionization energies but in terms of Slater's transition-state calculations in which half an electron is removed from the respective orbital.

5. Effective charges

The program used also provides a table of the values of the radial part of the wavefunctions of the 251 different values of position r. A fitting to a Slater form, by χ^2 minimization, provides us with the values of the effective charges. Let us recall that, for example,

$$R_{1s} = 2Z^{*3/2} \exp(-Z^*r) \tag{9}$$

is the radial part of the wavefunction for a 1s electron, where Z^* is the effective charge based on Slater's [35] rules. Clementi and Raimondi [36] proposed other values. Table 7 enables us to compare the respective values; for K our value is $Z^* = 18.5086$.

Table 7. Effective Z_{1s}^* charges: Z_s, Slater's values; Z_{C-R}, values obtained by Clementi and Raimondi; Z_{C-F}, our values.

	H							He
Z_s	1							1.70
Z_{C-R}	1.000							1.6875
Z_{C-F}	1.000							1.6815

	Li	Be	B	C	N	O	F	Ne
Z_s	2.70	3.70	4.70	5.70	6.70	7.70	8.70	9.70
Z_{C-R}	2.6906	3.6848	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
Z_{C-F}	2.6615	3.7179	4.6971	5.6766	6.6572	7.6403	8.6235	9.6067

	Na	Mg	Al	Si	P	S	Cl	Ar
Z_s	10.70	11.70	12.70	13.70	14.70	15.70	16.70	17.70
Z_{C-R}	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
Z_{C-F}	10.5973	11.5814	12.5673	13.5542	14.5431	15.5333	16.5245	17.5163

6. Exchange parameters for graphite intercalation compounds

We used these results to build [28] a crystal potential for the GICs [37] LiC_6, KC_8, etc.

On using Divincenzo's [38] proposal to construct approximate values of the crystal exchange parameters $\alpha_{crystal}$, a crystalline exchange parameter is calculated for different graphite intercalation compounds using

$$\alpha_{crystal} = (6\alpha_{atomic\,C} + \alpha_{atomic\,M})/7 \tag{10}$$

$$\alpha_{crystal} = (8\alpha_{atomic\,C} + \alpha_{atomic\,M})/9. \tag{11}$$

Table 8. GIC exchange parameters.

Compound	$\alpha_{crystal}$	Compound	$\alpha_{crystal}$
Graphite	0.864 99	EuC_6	0.849 61
LiC_6	0.848 64	YbC_6	0.863 04
CaC_6	0.841 12	KC_8	0.843 34
SrC_6	0.834 98	RbC_8	0.841 81
BaC_6	0.837 29	CsC_8	0.843 57
SmC_6	0.848 30		

Equation (10) is valid for MC_6 compounds and equation (11) for MC_8 first-stage GICs. Table 8 summarizes the results for the series of alkali GICs studied by our group and enables one to evaluate the exchange contribution to the potential of intercalation compounds.

7. Conclusion

For any atom other than those listed here, we can send, on written request, the values of α and the analytical equations of the atomic potential and of the radial part of the atomic functions.

The major interest in those results is to provide, for band calculation by the tight, binding method, wavefunctions and atomic potentials in an analytical and not a tabulated form.

The electronic properties of graphite are fairly well known. Since the planar hexagonal arrangement of atoms is preserved in the binary GICs (figure 4), albeit with a change in stacking sequence and the insertion of planes of intercalate atoms, it is certainly of interest to begin with the electronic properties of graphite [39].

This approach is perhaps of even greater relevance to the properties of dilute compounds. In this case, one can initially conjecture that many properties of the crystal are controlled by the 'graphite regions', far from the filled layers of intercalate atoms. These regions can then be treated within the 'rigid-band theory'.

Intercalation produces charge transfer [40]; the in-plane carbon–carbon distance varies from one GIC to another obtained with different alkali metals (table 1).

These considerations are sufficient to consider, at least provisionally, each first-stage GIC as a new material and to perform complete band calculations with the help of our preceding exchange parameter evaluations.

References

[1] Charlier A, Charlier M F and Fristot D 1989 *J. Phys. Chem. Solids* **50** 987–97
[2] Hérold A 1988 *Chemical Physics of Intercalation* vol 1, ed A P Legrand and S Flandrois (New York: Plenum) pp 1–43
[3] De Launay J 1956 *Solid State Physics* vol 2 (New York: Academic) pp 219–303
[4] Lang L *et al* 1991 *Proc. 20th Biennial Conf. on Carbon (CA, 23–28 June 1990)*, at press
[5] Born M and Mayer J E 1932 *Z. Phys.* **75** 1
[6] Schwarz K 1972 *Phys. Rev.* B **5** 2466
[7] Gupta H C, Malhotra S, Rani N and Tripathi B B 1986 *Solid State Commun.* **57** 263–4
[8] Harbola M K and Sahni V 1989 *Phys. Rev. Lett.* **62** 489
[9] Harbola M K and Sahni V 1989 *Phys. Rev.* B **39** 10 437
[10] Levy M and Perdew J P 1985 *Phys. Rev.* A **32** 2010
[11] Li Y, Harbola M K, Krieger J B and Sahni V 1989 *Phys. Rev.* A **40** 6084
[12] Krieger J B and Li Y 1989 *Phys. Rev.* A **39** 6052
[13] Jones R O and Gunnarsson O 1989 *Rev. Mod. Phys.* **61** 689
[14] Parr R G and Yang W 1989 *Density Functional Theory of Atoms and Molecules* (Oxford: Oxford University Press)
[15] Antoniewicz P R and Kleinman L 1985 *Phys. Rev.* B **31** 6779
[16] Perdew J P and Wang Y 1988 *Mathematics Applied to Science* ed J Goldstein, S Rosencrans and G Sod (Boston, MA: Academic)
[17] Kleinman L and Lee S 1988 *Phys. Rev.* B **37** 4634
[18] Sahni V, Gruenebaum J and Perdew J P 1982 *Phys. Rev.* B **26** 4371
[19] Perdew J P 1985 *Phys. Rev. Lett.* **55** 1665
[20] Chevary A and Vosko S H 1988 *Bull. Am. Phys. Soc.* **33** 238
[21] Herman F, Ortenburger I B and Van Dyke J P 1970 *Int. J. Quantum Chem.* S**3** 827
[22] Aashamar K, Luke T M and Talman J D 1978 *At. Data Nucl. Data Tables* **22** 443
[23] Talman D and Shadwick W F 1976 *Phys. Rev.* A **14** 36
[24] Becke A D 1986 *J. Chem. Phys.* **84** 4524
   De Pristo A E and Kress J D 1987 *J. Chem. Phys.* **86** 1452
   Ghosh S K and Parr R G 1986 *Phys. Rev.* A **34** 785
[25] Fischer C F 1977 *The Hartree–Fock Method for Atoms* (New York: Wiley); 1987 *Comput. Phys. Commun.* **16** 355
[26] Slater J C and Johnson K H 1972 *Phys. Rev.* **5** 844
[27] Wang Y, Perdew J P, Chevary J A, Macdonald L D and Vosko S H 1990 *Phys. Rev.* A **41** 78
[28] Charlier A, Fristot D, Charlier M F, Doyen S and Lang L 1990 *Carbon* **28** 251
[29] Lafon E E and Lin C C 1966 *Phys. Rev.* **152** 579
[30] Desclaux J P 1969 *Comput. Phys. Commun.* **1** 216
[31] Press W H, Flannery B P, Teukolsky S A and Vetterling W T 1985 *Numerical Recipes* (Cambridge: Cambridge University Press) p 499
[32] Cohen-Tannoudji C, Diu B and Laloë F 1973 *Mécanique Quantique* (Paris: Hermann) p 1129
[33] Pascal P 1959 *Nouveau Traité de Chimie Minérale* vol II (Paris: Masson) pp 1–70
[34] Herman F and Skillman S 1963 *Atomic Structure Calculations* (Englewood Cliffs: Prentice-Hall)
[35] Slater J C 1930 *Phys. Rev.* **36** 57
[36] Clementi E and Raimondi D L 1963 *IBM Research Note* NJ-27
[37] Charlier A, Fristot D and Charlier M F 1989 *Proc. 19th Biennial Conf. on Carbon (The Pennsylvania State University, 25–30 June 1989)* (University Park, PA: Pennsylvania State University) p 544
[38] Divincenzo D P 1980 *Thesis* University of Pennsylvania
[39] Charlier M F and Charlier A 1987 *Chem. Phys. Carbon* **20** 59–212
[40] Fristot D *et al* 1991 *Proc. 20th Biennial Conf. on Carbon (CA: 23–28 June 1990)* at press
[41] Hartree D R 1957 *The Calculation of Atomic Structure* (New York: Wiley)