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The *ab initio* computational basis of the angular overlap model and its phenomenological effectiveness in the 5f ion compounds

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Abstract. Both the fundamental assumptions of the angular overlap model (AOM) and its common simplifications are shown to have a sound basis in the *ab initio* calculations of the crystal-field effect in uranium (III), (IV), (V), neptunium (IV) and plutonium (IV) ions in various crystals. The traditional σ–π approach is confirmed as a well-aimed initial step towards an interpretation of the effect. The specific role of the δ-contribution as an important lattice-dependent correction indicates the necessity of its inclusion in the model. The practical two-step interpretation method that naturally emerges from the *ab initio* calculations is recommended. The effectiveness of the AOM for actinide ionic systems is illustrated using available phenomenological results. The universal character of the AOM parametrization and simple rules concerning the relationships between the parameters—their mutual hierarchy, spectrochemical ordering and the definite dependence on the metal ionization degree—are pointed out and discussed in the light of other phenomenological models including the Newman's twin superposition model.

1. Introduction

Interpretation of the spectroscopic and magnetic properties of the actinide compounds together with understanding their physico-chemical foundation and its consistent explanation is far from trivial and requires much experience, intuition and caution. The literature adduces a number of examples of essential changes in interpretation after introducing some new experimental or theoretical data. Usually, the available experimental data remain too scanty to ensure an unequivocal interpretation without any additional assumptions. The main parameters of the model Hamiltonian commonly used for localized electrons in crystals—the Slater parameters F^k and the spin–orbit coupling constant ζ—can be temporarily predicted on the grounds of their general regularities [1, 2]. This, however, will not deal with the crystal-field parameters which may vary drastically from compound to compound depending strongly on the metal-ion coordination geometry.

The angular overlap model (AOM) [3–7] is one of those simplified phenomenological models which provide a highly compact description of the crystal-field effect irrespectively of a particular crystalline structure. The AOM distinguishes itself from among different propositions of this type by its simplicity, clear physico-chemical foundations, flexibility for further simplifications and systematization and finally its undoubted

success in describing 3d and 4f electron systems [5–10]. However, little attention has been paid so far to its use in actinide compounds. The well known specificity of the electronic structure of the actinide ions inclines us to verify both the general AOM assumptions as well as the accuracy of the simplified versions of the model just as in the case of the 5f electron systems.

The physico-chemical foundations of the AOM and its general formulation were presented in the monograph by Gerloch, Harding and Wooley [7]. In contrast to the pioneering formulation of the model by Schäffer and Jørgensen [3, 4] and to further re-definitions [5, 6] the Gerloch *et al* concept of cellular partitioning of the space around the metal ion is fully consistent with the AOM phenomenology. This formulation, however, gives rise to some difficulties with the quantitative estimation of the AOM parameters from first principles. Therefore we start with a definition closer to the traditional one [5, 6]. Our discussion is based on the *ab initio* calculations of the crystal-field parameters for uranium compounds reported recently [11–13] and sup-plemented by original results. It concentrates on both the inherent limitations of the model and some practical aspects of the phenomenology. In particular we focus our attention on formulating an effective interpretative method, the first trial applications of which have just been published [14–17]. In this method the simplest one-parameter version of the AOM is applied first and then the constraints are relaxed step by step.

The review of the latest phenomenological results is utilized as an attempt at independent verification of the introduced approximations and illustration of some general regularities of the AOM parameters. Solution of some actual interpretative problems shows the effectiveness of the model. The model is faced with conventional crystal-field parametrization, the Newman's superposition model and the symmetry descent technique.

2. Formulation of the model

In comparison with the standard parametrization of the one-electron crystal-field po-tential the AOM is an approximation specialized to ionic systems. The idea was to find an effective and simple phenomenological model. The initial concept of a local Wolfsberg–Helmholtz-like potential [3, 4] has been extended taking into account the transformational properties of open shell orbitals and the perturbation approach to the actual many-electron problem based on the projection operator method and the Löwdin partitioning technique [5–7]. The conventional definition of the AOM is based on the following three assumptions:

(i) The crystal-field potential seen by the unpaired electrons of the metal ion is produced only by its nearest neighbours—ligands.

(ii) Each ligand t gives an independent additive contribution v_t and the resulting potential

$$V = \sum_t v_t \tag{1}$$

holds the metal site symmetry.

(iii) The local symmetry of v_t along the metal–ligand axis is $C_{\infty v}$. As we will see later this assumption may be weakened in generalized versions of the AOM.

In fact, none of these assumptions is fulfilled precisely. The consequences of some approximations are worth further investigation. We will return to them in section 3.

The basic idea of the AOM approach is to conceive the crystal-field potential V as a superposition of several independent contributions v_t determined by the geometry of the metal ion surroundings. Instead of the global crystal-field parameters B_q^k we have, at our disposal, local parameters attributed to the separated contributions. Naturally, the contributions v_t in the traditional formulation are associated with the ligands.

According to (1) and the transformational properties of the central metal orbitals under rotation the relationship between the matrix elements of the global crystal-field potential V and the matrix elements of single ligand potential v_t within the function space truncated to 5f orbitals, $|m\rangle \equiv |5fm\rangle$, reads

$$\langle m|V|m'\rangle = \sum_t \sum_\mu \sum_{\mu'} D_{\mu m}^{(3)*}(t) D_{\mu' m'}^{(3)}(t) e_{\mu\mu'}^t \qquad (2)$$

$$e_{\mu\mu'}^t \equiv \langle \mu|v_t|\mu'\rangle_t \qquad (3)$$

where m and μ are magnetic quantum numbers in the global and local coordinate systems respectively. The index t on the bracket means that the integral is calculated in the local metal–ligand t coordinate system the z_t-axis of which is directed towards the metal–ligand axis. $D_{\mu m}^{(3)}(t) \equiv D_{\mu m}^{(3)}(\Phi_t, \Theta_t, 0)$ is the third-rank rotation matrix element; Θ_t, Φ_t are the angular coordinates of ligand t in the central coordinate system. Comparing (2) with the matrix elements of the conventional crystal-field potential,

$$V = \sum_{k,q} B_q^k C_q^k \qquad (4)$$

one obtains

$$B_q^k = \sum_p \sum_t b_{kp}^t D_{pq}^{(k)*}(t) \qquad (5)$$

where

$$b_{kp}^t = \frac{2k+1}{7}\left[\begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}\right]^{-1} \sum_{\mu\mu'}(-1)^\mu \begin{pmatrix} 3 & k & 3 \\ -\mu & p & \mu' \end{pmatrix} e_{\mu\mu'}^t \qquad (6)$$

and $\begin{pmatrix} \cdots \\ \cdots \end{pmatrix}$ denotes the usual 3j symbol.

Assumption (iii) causes $e_{\mu\mu'}^t$ or b_{kp}^t to be equal to zero for $\mu \neq \mu'$ or $p \neq 0$ respectively. The diagonal elements $e_\mu^t \equiv e_{\mu\mu}^t$ are the usual AOM parameters. Since the matrix $\langle m|V|m'\rangle$ is Hermitian and invariant under time reversal, e_μ must be real and $e_\mu = e_{-\mu}$. Furthermore, since the experimental data are related to the energy level differences only the diagonal matrix elements of V are determined to within some constant corresponding to a choice of zero energy. So, one of the e_μ parameters can be set equal to zero without loss of generality. The natural choice is to put $e_{\pm 3} = 0$. Therefore only three independent parameters remain effective: e_σ^t, e_π^t and e_δ^t for $|\mu| = 0, 1$ and 2 respectively. Accordingly, equations (2), (5) and (6) simplify to the following forms:

$$\langle m|V|m'\rangle = \sum_t \sum_{\mu=-2}^{2} D_{\mu m}^{(3)*}(t) D_{\mu m'}^{(3)}(t) e_{|\mu|}^t \qquad (7)$$

$$B_q^k = \sum_t C_q^{k*}(\Theta_t, \Phi_t) b_k^t \qquad (8)$$

where

$$b_2 = \tfrac{5}{7}e_\sigma + \tfrac{15}{14}e_\pi$$
$$b_4 = \tfrac{9}{7}e_\sigma + \tfrac{3}{7}e_\pi - 3e_\delta \tag{9}$$
$$b_6 = \tfrac{13}{7}e_\sigma - \tfrac{39}{14}e_\pi + \tfrac{39}{35}e_\delta.$$

The index t distinguishing ligands is omitted in (9) for clarity.

The intrinsic parameters e_μ or b_k depend on the metal–ligand distance only, but not on angular coordinates of the ligand. Therefore, as seen from (8), the ratios of the B_q^k parameters of the same order k are definitely fixed for the clusters of equidistant ligands. This is a characteristic consequence of the superposition assumption (ii).

Equation (7) is the basic AOM formula. In practice it is sufficient to evaluate the elements of rotation matrices $D_{\mu m}^{(3)}(\Phi_t, \Theta_t, 0)$ and decouple the resultant crystal-field matrix elements within the 5f^n function basis into the one-electron matrix elements, $\langle m|V|m'\rangle$.

It is worth noting that equation (2) may be considered as a generalization of equation (7) to an arbitrary local symmetry of the metal–ligand bond. It extends applicability of the model to systems of strongly polarized ligands or ligands of complex structures where assumption (iii) is not fulfilled. Since the $e_{\mu\mu'}$ matrix can always be put in diagonal form by a unitary transformation the whole procedure developed for linear ligators remains valid.

3. AOM in the light of the *ab initio* calculations

Our present aim is to look at the AOM from the *ab initio* calculation point of view. The theoretical model of the crystal-field which we follow (see [7] and [11] for details) grows naturally from the quantum many-body approach. The group product function formalism and the projection operator technique have been used to obtain a perturbation expansion of the Hamiltonian of the 5f electron subsystem. The effective one-electron crystal-field potential has been extracted from this expansion, cut-off at second-order terms. It consists of a number of contributions of varying origin: the electrostatic interaction of lattice charge density; the interionic exchange interaction; the renormalization terms arising from the non-orthogonality of the free-ion orbitals— M(5f)-L(ns, np) (contact covalency), M(6s, 6p)-L(ns, np) (contact shielding), L(ns, np)-L'(ns, np), contact polarization—and analogical terms arising from one-electron excitations—L→M (covalency), M→M (shielding) and both L→L and M'→M' (polarization). In the present discussion we use the previous results obtained with this model for some ionic 5f electron complexes [11–13, 15] and the complementary calculations performed for M-L systems where M ≡ $U^{3+}, U^{4+}, U^{5+}, Np^{4+}, Pu^{4+}$ and L ≡ $O^{2-}, F^-, Cl^-, Br^-, I^-$ for various metal–ligand distances. The free-ion wavefunctions and energies have been obtained with the standard Dirac–Slater procedure. The shielding effect has been estimated using Sternheimer's shielding factors for the U^{4+} ion [18].

3.1. Limitations to the AOM

Some of the crystal-field mechanisms mentioned earlier do not obey the AOM assumptions. We concentrate here only on the most important contributions provided by

the second-order perturbation theory. First of all it concerns the direct electrostatic interactions of further neighbours and multipoles induced on ligands. The contribution of the induced multipoles to the crystal-field parameters may be obtained from the multipole expansion of the lattice charge density potential by means of the tensor operator technique and $n - j$ symbols algebra [19]. It reads

$$
B_q^k\big|_{\substack{\text{induced}\\ \text{multipoles}}} = -\langle r^k\rangle \sum_{t,n,\mu}(-1)^k \left\{ \frac{(2k + 2n + 1)!}{2^n(2k)!}\right\}^{1/2}
$$

$$
* \begin{pmatrix} k & n & k+n \\ -\mu & \mu & 0 \end{pmatrix} \frac{1}{R_t^{k+n+1}} M_{t-\mu}^n D_{\mu q}^{k^*}(\Phi_t,\Theta_t,0) \tag{10}
$$

where M_t^n is the induced $2n$-pole moment expressed in the local metal–ligand t coordinate frame, $n = 1,2\ldots$, corresponds to dipole, quadrupole and so on, μ runs over their components, R_t, Θ_t, Φ_t are the polar coordinates of ligand t, $\langle r^k\rangle$ is the mean value of r^k in the 5f state. If the free-ion polarization tensors are known the induced multipoles M_t^n may be determined from the lattice electrostatic equilibrium equations (see [20]).

The ligand contribution corresponding to the multipole moment components along the metal–ligand axis is consistent with the AOM assumptions. The *non-axial* part, being of present interest, may be calculated according to equation (10) with the summation limited to terms with $\mu \neq 0$. The results obtained for several different uranium compounds are listed in table 1 in the rows denoted by LP and they may be compared with the global electrostatic contributions of further neighbours (FN). A tendency towards mutual compensation is observed. Both mechanisms mainly modify only the second-order parameters B_q^2 for which the shielding by the external uranium electrons is very strong (about 90%). Therefore their actual influence is moderate.

The FN contribution is not included in the model by definition but from the phenomenological point of view such an elimination is purely artificial. According to the symmetry of the central-ion environment the FN contribution may be reproduced within the AOM parametrization scheme in the respective part. In high symmetry systems, e.g. UO_2 (see table 1), it is fully reproducible! The Gerloch *et al* concept of cellular partitioning [7] allows one to avoid this inconsistency if cells are thought to contain a sufficient number of FNs. Alternatively, the definition ((i)–(iii)) may simply be generalized by extending the model term 'ligand' to some conceptual crystal object which also represents the specified part of the FN contribution.

The so-called *contact shielding* (CS) is the third, apart from the FN and non-axial polarization contributions, important off-AOM mechanism specified in table 1. It is the mechanism originating from renormalization resulting from the non-orthogonality of the outer uranium wavefunctions 6s and 6p (ξ_ν) and the ligand wavefunctions ns, np (χ_τ^t), where ν, τ denote nlm quantum numbers and t enumerates the ligands. The off-AOM part of the contact shielding potential has the form:

$$
V^{CS} = \sum_{t,\tau}\sum_{\nu}\langle \chi_\tau^t|\xi_\nu\rangle^2[2J(\xi_\nu,\xi_\nu) - K(\xi_\nu,\xi_\nu)] \tag{11}
$$

where J and K denote the Coulomb and exchange operators respectively and $\langle\chi_\tau^t|\xi_\nu\rangle$ is the overlap integral. V^{CS} in equation (11) is a correction to the Coulomb intra-ionic interaction between the 5f and the outer metal electrons induced by the previously mentioned non-orthogonality.

Table 1. Main off-AOM contributions to the crystal-field parameters for chosen uranium compounds (in cm^{-1}): FN, further neighbours; LP, non-axial dipole and quadrupole ligand polarization; SH, shielding of FN + LP contributions; CS, contact shielding. Their sum $\Sigma = $ FN + LP + SH + CS; and T is the total calculated value including both the AOM-consistent contributions and Σ.

cm^{-1}		B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	
UO$_2$	FN		640	390	110	−210	
	LP		0	0	0	0	
	SH		−30	−20	10	−20	
	CS		0	0	0	0	
	Σ		610	370	120	−220	
	T		−7140	−4270	2890	−5410	
UCl$_4$	FN	800	80	230	−20	10	
	LP	−1402	−81	−327	265	−167	
	SH	535	0	4	11	−7	
	CS	−420	0	0	0	0	
	Σ	−486	−1	−99	256	−163	
	T	−1370	2210	−6330	−710	310	

		B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6
CsUF$_6$	FN	−1390	−130	−170	0	0	0
	LP	575	−18	−23	−111	89	−6
	SH	725	6	8	−5	4	0
	CS	280	0	0	0	0	0
	Σ	190	−142	−185	−116	93	−6
	T	640	−17410	19290	3670	3810	2640
Cs$_2$UCl$_6$	FN	740	20	−60	−10	10	−10
	LP	−670	88	−2	42	63	10
	SH	−62	−5	3	1	3	0
	CS	−360	0	0	0	0	0
	Σ	−352	103	−59	33	76	0
	T	−680	−4960	−7350	2070	−40	1210

It may be shown [21] that the only crystal-field parameter influenced by this mechanism is B_0^2 which is equal to

$$B_0^2 = \sum_t C_0^2(t) S^t [\tfrac{4}{5} F^2(6p, 5f) - \tfrac{9}{35} G^2(6p, 5f) - \tfrac{5}{65} G^4(6p, 5f] \qquad (12)$$

where F^2, G^2, G^4 are the usual Condon–Shortley parameters and $S^t = \langle \chi_{tns} | \xi_\sigma \rangle_t^2 + \langle \chi_{tnp\sigma} | \xi_\sigma \rangle_t^2 - \langle \chi_{tnp\pi} | \xi_\pi \rangle_t^2$.

The results of calculations based on equation (12) are presented in rows CS of table 1. It is seen that the CS off-AOM contribution reaches as much as 50% of the total value of the B_0^2 parameter. It should, however, be noted that in the case when, due to symmetry restrictions, there is at most one non-zero second-order parameter the effect is not detectable by the AOM phenomenology. Anyway, in general, the CS is an important off-AOM mechanism which should be taken into consideration in each particular case.

The non-orthogonality of orbitals belonging to different ligands leads to the so-called contact polarization potential which also originates in renormalization. Its

off-AOM part reads

$$V^{\text{c.pol}} = \sum_{t,\tau} \sum_{\substack{t'\tau' \\ t'\neq t}} \langle \chi_\tau^t | \chi_{\tau'}^{t'} \rangle^2 [2J(\chi_{\tau''}^{t'}\chi_\tau^t) - K(\chi_{\tau''}^{t'}\chi_\tau^t)]. \tag{13}$$

This is a ligand–ligand exchange charge potential [22]. In spite of the relatively large ligand–ligand overlap integrals $V^{\text{c.pol}}$ is of secondary meaning due to the almost perfect cancellation of the direct and exchange terms.

Several higher-order mechanisms in the perturbation approach also do not obey the AOM assumptions but they may probably be neglected (see the estimation of one of the most important third-order corrections for $PrCl_3$ given in [23]).

The summarized off-AOM contributions (Σ) shown in table 1 are in general much smaller than the total calculated B_q^k parameters (T). The only exceptions occur when the geometrical factors for groups of equivalent ligands (see equation (8)),

$$G_q^k = \sum_t C_q^{k^*}(\Theta_t, \Phi_t) \tag{14}$$

are relatively small due to the compensation effect—the case of G_0^2 for $CsUF_6$ and Cs_2UCl_6 and G_3^6 for Cs_2UCl_6, or if there are few competing groups of equivalent ligands as in G_0^2 and G_6^6 for UCl_4, see table 2. In other words the characteristic domination of the AOM contributions may be hidden for a given B_q^k parameter due to the specific geometry of the coordination cluster. As a consequence the AOM parameters fitted to the crystal-field energy levels may be wrongly determined. Evaluation of the geometrical factors and their careful analysis allows one to anticipate such an instance and avoid overhasty conclusions drawn from the formal AOM interpretation.

Table 2. Geometrical factors G_q^k.

		G_0^2	G_0^4	G_4^4	G_0^6	G_4^6	
UO_2			−3.111	−1.859	1.778	−3.326	
UCl_4[a]	(1)	2.224	−0.384	−0.184	−1.684	−0.828	
	(2)	−1.728	0.852	−1.904	−0.212	0.640	

	G_0^2	G_0^4	G_3^4	G_0^6	G_3^6	G_6^6
$CsUF_6$	0.195	−2.429	−2.739	1.092	−1.073	0.765
Cs_2UCl_6	−0.478	−1.993	1.912	1.790	0.068	1.063

[a] There are two interpenetrating tetrahedra of various U–Cl distances.

3.2. Putting this into practice

The number of the AOM parameters is equal to $3N$ where N is the number of groups of non-equivalent ligands. Clearly, the parameters representing the strength of the metal–ligand interaction undergo some inherent limitations. The original formulation developed for the transition metal complexes [3, 4] assumes the ligand field to be a first-order perturbation of the Wolsberg–Helmholtz type. In consequence the crystal-field energy and the AOM parameters are expressed in terms of the overlap integrals and unperturbed metal and ligand energies. Although this is undoubtedly a

Table 3. Covalency and contact covalency contributions, C, to the axial crystal-field parameters compared with total, T, and experimental, E, values (in cm^{-1}).

		B_0^2	B_0^4	B_0^6	Ref.
UO$_2$	C		−12130	5070	[12]
	T		−7140	2890	[12]
	E		−8360	3600	[24]
			−6690	2560	[12]
CsUF$_6$	C	1000	−16310	4280	[11]
	T	640	−17410	3670	[11]
	E	880	−17870	4370	[25]
		430	−14210	3600	[26]
		700	−14590	3040	[16]
Cs$_2$UCl$_6$	C	−830	−4470	2230	[11]
	T	−680	−4960	2070	[11]
	E	—	−4810	2430	[27]
UCl$_4$	C	−1350	1840	−1670	[11]
	T	−1370	2210	−710	[11]
	E	−1010	1730	−2700	[28]

Table 4. Theoretical values of e_μ in relation to square overlap integrals S_μ^2 for UCl$_4$.

U–Cl dist. (Å)	e_s (cm^{-1}	$e_{p\sigma}$ (cm^{-1})	$e_{p\pi}$ (cm^{-1})	$c_s = e_s/S_s^2$ ($\times 10^5$ cm^{-1})	$c_{p\sigma} = e_{p\sigma}/S_{p\sigma}^2$ ($\times 10^5$ cm^{-1})	$c_{p\pi} = e_{p\pi}/S_{p\pi}^2$ ($\times 10^5$ cm^{-1})
2.65	742	1150	710	6.50	6.85	6.79
2.88	324	657	355	5.89	6.29	6.94

crude approximation the predicted correlation between the AOM parameters and the overlap integrals has been widely confirmed for both transition and lanthanide metal compounds [5–10]. The question is whether it is true for the 5f electron systems.

The *ab initio* calculations based on the model outlined at the beginning of this section show that the sum of only two contributions to the crystal-field parameters, namely the covalency and the contact covalency, is almost adequate for the whole effect [11–13]. This is illustrated in table 3. The AOM parameters corresponding to these mechanisms, e_σ and e_π, are approximately proportional to the respective square overlap integrals and e_δ is equal to zero if ligands have no occupied d orbitals:

$$e_\sigma = e_s + e_{p\sigma} \simeq c_s S_s^2 + c_{p\sigma} S_{p\sigma}^2 \simeq c(S_s^2 + S_{p\sigma}^2) \qquad e_\pi \simeq c_{p\pi} S_{p\pi}^2 \simeq c S_{p\pi}^2 \qquad e_\delta = 0.$$

$$(15)$$

c_μ is the proportionality coefficient depending on averaged energies of the metal 5f and ligand $\mu = ns, np\sigma, np\pi$ orbitals, $S_\mu = \langle 5f|\mu\rangle$ is the inter-ionic overlap integral calculated in the local coordinate system. The accuracy of the approximation:

$$c_s \simeq c_{p\sigma} \simeq c_{p\pi} \equiv c \qquad (16)$$

introduced in equations (15) is illustrated using UCl$_4$ as an example in table 4. Table 4 also shows that the coefficients c_μ only weakly depend on the metal–ligand distance

and therefore the dependence on distance of both the e_σ and e_π parameters and their ratio may well be approximated by the square overlap integrals (see table 5):

$$e_\mu(R) = c_\mu S_\mu^2(R) \qquad \mu = \sigma, \pi \tag{17}$$

where

$$S_\sigma^2 = S_s^2 + S_{p\sigma}^2. \tag{18}$$

It is convenient to express the dependence (17) in the form of a simple power function,

$$e_\mu(R) \simeq (R_0/R)^{\alpha_\mu} e_\mu(R_0) \tag{19}$$

where R_0 is a reference distance which may be taken as equal to the average distance within the coordination cluster. The values of the exponents α_σ and α_π and the ratio e_π/e_σ estimated from the overlap integrals for various actinide–ligand systems are given in table 6. Their dispersions from the mean values are moderate. The exponents and ratios are close to the values commonly accepted for lanthanide ions [8].

Table 5. Distance dependence of e_μ parameters and corresponding square overlap integrals for UCl$_4$.

	$\mu = s$	$\mu = p\sigma$	$\mu = p\pi$
$e_\mu(R = 2.65 \text{ Å})/e_\mu(R = 2.88 \text{ Å})$	2.29	1.75	2.00
$S_\mu^2(R = 2.65 \text{ Å})/S_\mu^2(R = 2.88 \text{ Å})$	2.28	1.60	2.05

3.3. Role of the e_δ parameter

Equations (15)–(19) define the simplest, common, one-parameter version of AOM, say AOM-I. Tables 3–5 illustrate its accuracy. Much of today's criticism about the AOM refers, as a matter of fact, to this version [29]. The AOM-I is based on and reflects the essential renormalization terms which do not contribute to the e_δ parameter by definition. Thus the e_δ may be treated as a measure of the remaining contributions.

The most important contributions to e_δ calculated for UCl$_4$ are shown in table 7. They are mutually competing and strongly dependent on the metal–ligand distance. Their sum is negative for the smaller distance and positive for the larger one. What should be emphasized is the large contribution made by the dipolar and quadrupolar polarization to the e_δ parameter, especially for smaller R. The polarization effect is non-local in origin, i.e. it comes from the interaction of the whole crystal lattice. That is why e_δ is markedly individualized and does not obey any ligand systematization.

In the absence of the polarization effect some regularities are observed. The shielded contribution of the unpolarized ligand charge density as a function of M–L distance for U^{4+}–O^{2-} and U^{4+}–Cl$^-$ systems is shown in figure 1. Similarly as before it may be approximated according to equation (19). The exponents obtained for several examples are given in table 6. For practical use their mean value (8.45) may be accepted temporarily.

Table 6. Distance dependence of e_μ approximated by power function $e_\mu(R) = e_\mu(R_0)(R_0/R)^{\alpha_\mu}$ for R within the range $R_0 \pm 0.1$ Å, where R_0 is sum of the respective ionic radii. Averaged values of the exponents α_μ and the ratios e_π/e_σ.

Metal	Ligand	R_0	α_σ	α_π	α_δ	e_π/e_σ
U^{5+}	F^-	2.09	6.55	7.91	8.63	0.350
	Cl^-	2.61	7.13	8.85		0.324
	Br^-	2.78	7.36	9.09		0.323
	I^-	2.99	7.25	9.16		0.321
	O^{2-}	2.23	6.92	7.98		0.319
U^{4+}	F^-	2.33	6.78	7.98		0.347
	Cl^-	2.78	6.97	8.74	8.78	0.334
	Br^-	2.92	7.03	8.83		0.340
	I^-	3.13	6.91	8.93		0.337
	O^{2-}	2.37	6.71	7.59	7.10	0.339
Np^{4+}	F^-	2.31	6.94	8.12		0.339
	Cl^-	2.76	7.13	8.85		0.328
	Br^-	2.90	7.18	8.94		0.333
	I^-	3.11	7.07	9.03		0.331
	O^{2-}	2.35	6.85	7.73		0.331
Pu^{4+}	F^-	2.29	7.06	8.23		0.335
	Cl^-	2.74	7.25	8.95		0.323
	Br^-	2.88	7.32	9.03		0.328
	I^-	3.09	7.20	9.11		0.325
	O^{2-}	2.33	6.96	7.85		0.326
U^{3+}	F^-	2.47	6.14	7.31		0.385
	Cl^-	2.92	6.23	8.08		0.377
	Br^-	3.06	6.27	8.18	9.27	0.386
	I^-	3.27	6.12	8.33		0.380
	O^{2-}	2.51	6.15	6.81		0.385
Mean value			7.12	8.28	8.45	0.343

Table 7. Basic contributions to e_δ for UCl_4 (in cm^{-1}).

	e_δ	
	$R = 2.65$ Å	$R = 2.88$ Å
Unperturbed ligand charge density:		
core: nucleus+inner electrons[a]	161	4
Coulomb direct of outer electrons[a]	17	90
Coulomb exchange of outer electrons	−96	−51
Ligand polarization[a,b]	−232	−24
Total	−150	20

[a] Shielded contribution.
[b] AOM-consistent part only.

Unfortunately, approximation (19) is not valid for e_δ when the ligand polarization becomes important as in UCl_4 (see table 7). A more general approximation might
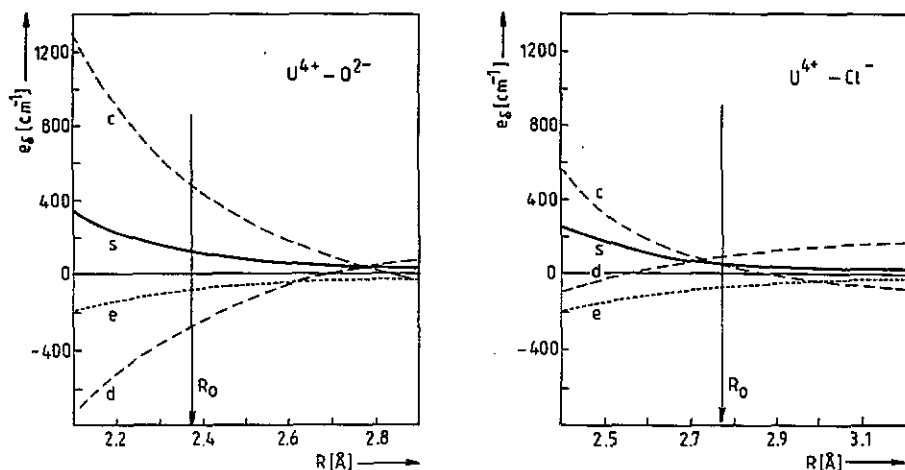
Figure 1. Distance dependence of the shielded contribution to e_δ of unperturbed ligand charge density (s) and its components: direct (d), exchange (e) and core (c) for $U^{4+}-O^{2-}$ and $U^{4+}-Cl^-$ systems.

have the following two-term form:

$$e_\delta(R) = \left(\frac{R_0}{R}\right)^{\alpha_\delta^+} e_\delta^+ + \left(\frac{R_0}{R}\right)^{\alpha_\delta^-} e_\delta^- \tag{20}$$

where e_δ^+ and e_δ^- correspond to the positive and negative contributions, respectively. From the data of table 7 for UCl_4 and $R_0 = 2.65$ Å one obtains

$$
\begin{aligned}
e_\delta^+ &= 173 \text{ cm}^{-1} & \alpha_\delta^+ &= 7.8 \\
e_\delta^- &= -328 \text{ cm}^{-1} & \alpha_\delta^- &= 17.6.
\end{aligned}
\tag{21}
$$

Approximation (20) is not very convenient from a practical point of view since it needs as many as four parameters—e_δ^+, e_δ^-, α_δ^+, α_δ^-—and it is hard to indicate any correlation between them which would be universal in character. This example is a warning against a routine approach to the $e_\delta(R)$ dependence. On account of the competitive contributions, each such dependence has its own individual character and may be roughly approximated by the simple power form within the narrow range of R and exotic exponent. Approximation (19) is useless when $e_\delta^+ \simeq -e_\delta^-$, i.e. when $e_\delta(R_0) \simeq 0$.

4. Phenomenological effectiveness of the AOM—review of the recent results

It has been shown in the previous section that the AOM is firmly founded by the results of the *ab initio* calculations of the crystal-field effect in the ionic actinide compounds. If approximation (19) is extended to e_δ the basic AOM equation (7) may be rewritten in the following form:

$$\langle m|V|m'\rangle = \sum_{\mu=0}^{2} K_{mm'}^\mu e_\mu \tag{22}$$

where $K^{\mu}_{mm'}$ is the coordination factor

$$K^{\mu}_{mm'} = \sum_t (2 - \delta_{\mu 0}) D^{(3)*}_{\mu m}(t) D^{(3)}_{\mu m'}(t) (R_0/R_t)^{\alpha_{\mu}} \tag{23}$$

R_0 is the reference distance and $e_{\mu} \equiv e_{\mu}(R_0)$.

On the ground of the revealed relationship linking the AOM parameters two simplified versions of the model have been postulated:

AOM-I With only one free parameter, e_{σ}, and the following constraints:

$$e_{\pi} = (S^2_{\pi}/S^2_{\sigma})e_{\sigma} \qquad e_{\delta} = 0.$$

AOM-II With two free parameters, e_{σ} and e_{δ}, and the constraint:

$$e_{\pi} = (S^2_{\pi}/S^2_{\sigma})e_{\sigma}$$

where S^2_{σ} and S^2_{π} are the squares of the overlap integrals defined in section 3.2.

Relaxing the e_{π}/e_{σ} ratio but maintaining approximation (19) leads back to the three-parameter model, AOM-III or simply AOM.

The present question is how these models work in practice in actinide systems.

4.1. Conventional approach—AOM-I

The AOM has not been very popular in the interpretation of crystal-field effects in actinide compounds. Nevertheless, some recent trials of its application to the uranium compounds [14–17, 30] are encouraging and instructive. First of all, they indicate that even the simplest one-parameter version of the model, AOM-I, allows the crystal-field effect in any uranium compound to be predicted fairly well. The AOM-I seems to be the most suitable approach for a preliminary interpretation of new data. When the e_{σ} parameter for a given metal–ligand bond is known beforehand then its value extrapolated according to equation (19) for actual distance(s) in the coordination cluster is a good approximation with which to start. The simultaneous fitting of the energy spectra observed for different compounds of the same metal–ligand bond, by means of one AOM-I parameter only is also possible. Such calculations have been successfully performed for the U^{4+}–Cl^-, U^{4+}–Br^- and U^{5+}–F^- bonds in the following groups of compounds: $\{U^{4+}:\alpha\text{-}ThCl_4, U^{4+}:\beta\text{-}ThCl_4, UCl_4\}$ [14], $\{U^{4+}:\alpha\text{-}ThBr_4, U^{4+}:\beta\text{-}ThBr_4\}$ [14] and $\{CsUF_6, \alpha\text{-}UF_5, \beta\text{-}UF_5\}$ [16], respectively.

Independently, a natural regularity in the AOM parameters expected on the grounds of the physico-chemical arguments opens new possibilities of prediction and verification of the crystal-field effect. Phenomenological data quoted in table 8 convey an idea of it. As is seen, the e_{σ} parameter strongly depends on the ionization degree of the uranium: it is of order of 500 cm^{-1} for U^{3+} and three and seven times larger for U^{4+} and U^{5+}, respectively. The spectrochemical ordering of ligands is also reproduced here but the observed dependence is relatively weak.

The same rules are in force for the e_{π} parameter. It takes the value of about $e_{\sigma}/3$ which agrees well with that estimated on the ground of the overlap integrals.

Table 8. AOM parameters for uranium (III), (IV) and (V) ionic compounds (in cm^{-1}).

Compound	Point group	U–L av. dist.(Å)	e_σ	e_π	e_δ	Ref.
UCl$_3$	C$_{3h}$	2.932	596	226	32	[15]
UBr$_3$	C$_{3h}$	3.090	459	177	24	[15]
UI$_3$	C$_{2v}$	3.277	461	166	63	[15]
U^{4+}:ThSiO$_4$	D$_{2d}$	2.417	1650	550	370	[14]
U^{4+}:β-ThCl$_4$	D$_{2d}$	2.806	1400	650	300	[14]
U^{4+}:β-ThBr$_4$	D$_{2d}$	2.986	1210	420	280	[14]
CsUF$_6$	D$_{3d}$(O$_h$)	2.057	3380	1090	−400	[16]
α-UF$_5$	D$_{4h}$	2.077	4150	1340	0	[16]
			5523	1337		[30]
β-UF$_5$	C$_2$(D$_{4d}$)	2.190	2600	840	430	[16]
			3816	1053		[30]

4.2. Refinement

The AOM-II switching on the e_δ parameter allows the results obtained with AOM-I to be improved. Table 8 shows that the e_δ parameter reaches values of the order of 10–20% of the dominating e_σ. This indicates the magnitude of the expected correction of the fitting results gained with this parameter.

As has been pointed out in section 3.3, within the generalized model taking into account the whole metal ion environment, e_δ may depend on crystal structure via polarization and other non-local effects. That is why the spectrochemical ordering seen in table 8 is only reproduced by the e_δ values for the isostructural compounds.

In table 8 the e_δ parameter is positive as a rule but the example of the uranium (V) fluorides shows that it may also reach negative values, even fairly large ones. The strong increase of e_δ observed for the U^{5+}–F$^-$ bond from negative to positive values agrees qualitatively with the theoretical dependence of e_δ on the M–L distance in the absence of polarization effects (figure 1). In general, e_δ, in contrast to e_σ and e_π, can hardly be estimated on the ground of some broad rules. As table 8 shows it should be treated independently in each individual case. The enigmatic role of the e_δ parameter has probably been the reason for the very limited interest shown in it so far.

In all the considered examples, the relaxation of the fixed e_π/e_σ ratio and, as a consequence, the free variation of all three parameters have only a slight, if any, influence on the fitting results. This observation proves the adequacy of the square overlap integral scaling (equation (15)).

4.3. Solvable problems

Scarce experimental data, low symmetry of the metal ion site, lattice distortion connected with magnetic phase transition, applied hydrostatic pressure, incommensurate phases—all these situations, which are frequently met in actinide materials, give rise to serious interpretative problems in the traditional approach. But, as is shown later, this is just the right field for applying the AOM because fortunately the number of physically acceptable solutions is clearly confined.

In β-UF$_5$, for example, only four electronic transitions have been observed [30] and in fact they ought to be interpreted in terms of sixteen independent parameters:

the spin–orbit coupling constant and fifteen C_2 crystal-field parameters. The initial interpretation [30] was based on the idealized uranium (5+) site symmetry to the D_{4d} point group and, as a consequence, on a reduced number, three, of independent crystal-field parameters B_q^k—the axial ones. Clearly, the four-parameter fitting to four levels had to be and was exact. The alternative AOM-I and AOM-II interpretations for the actual point symmetry (C_2) also turned out to be satisfactory, although the number of effective parameters was reduced to one and two, respectively (e_μ instead of B_q^k) [16]. The magnitude of the non-axial crystal-field parameters previously ignored and the discrepancy between the two sets of axial ones brings into question the validity of the symmetry idealization technique.

The case of the U^{4+} ion doped into β-ThCl$_4$ and β-ThBr$_4$ hosts well illustrates the AOM ability for reproducing the crystal-field variations induced by small distortions of the coordination polyhedron [14]. It was possible due to the unique observation and interpretation of site selective excitations in the incommensurate phases of these crystals [31]. If the symmetry of the soft optic branch is τ_4 [32] and the modulation has a sinusoidal character the displacement of tth ligand in the lth primitive unit cell is given by the following expression [32]:

$$u_{lt} = \eta e_t \cos(\phi_l + q \cdot R_t - \theta_t) \tag{24}$$

where R_t is the position vector of the ligand t within the cell; q, the modulation wavevector, e_t a unit vector perpendicular to q, η, an amplitude factor, θ_t, t-dependent phase factor and

$$\phi_l = q \cdot l (\text{modulo } \pi) \qquad |\phi_l| \leqslant \pi/2 \tag{25}$$

is a cell-dependent phase factor. Practically, ϕ_l may take any value from the range $-\pi/2$ to $+\pi/2$. The displacement (24) lowers the thorium ion point symmetry from D_{2d} to C_2 except for $\phi_l \simeq 0, \pm\pi/2$ corresponding to D_{2d} and D_2 site symmetries, respectively. It can be shown that the observed spectral singularities originate from these special cells [33]. Making the substitution

$$R_t \rightarrow R_t + u_{lt} \tag{26}$$

in equation (7) or (8) allows one to estimate the crystal-field matrix elements or B_q^k parameters as a function of ϕ_l. In particular, one can reproduce the B_q^k parameters corresponding to the distinguished phases 0 and $\pm\pi/2$ using the e_μ parameters evaluated from the well resolved spectra of the commensurate phases. The B_q^k parameters generated by the $D_{2d} \rightarrow D_2$ distortion ($\phi_l = \pm\pi/2$) are compared in table 9 with those obtained independently by direct fitting of the incommensurate phase spectra [34, 35]. As is seen the best agreement takes place for the modulation amplitude η equal to 0.020 and 0.015 Å for the β-ThCl$_4$ and β-ThBr$_4$ matrices respectively which are consistent with those anticipated independently [32]. The analogical example of the AOM ability to reproduce the crystal-field dependence on small changes of the coordination geometry for Pr^{3+}-doped rare earth trichlorides was presented recently [9].

In many cases the ambiguity of the traditional parametrization makes the proper interpretation of the crystal-field effect difficult. Then the AOM is a convenient tool for verifying some artificial and unphysical solutions. For example, the position of the level invisible in the inelastic neutron scattering spectra of the UBr$_3$ and UI$_3$ is

Table 9. Variation of the D_2 crystal-field parameters of uranium (IV) ion doped in incommensurate β-ThCl$_4$ and β-ThBr$_4$ host crystals with the modulation amplitude, η; comparison with the experimental values, E (in cm^{-1}).

		B_2^2	B_2^4	B_2^6	B_6^6
β-ThCl$_4$	E	-80	360	160	420
		±50	±170	±170	±220
	$\eta = 0.010$	-50	210	140	160
	$\eta = 0.020$	-90	410	280	320
	$\eta = 0.030$	-140	610	410	470
β-ThBr$_4$	E	-80	320	140	120
		±30	±120	±100	±130
	$\eta = 0.005$	-40	80	80	140
	$\eta = 0.015$	-120	230	240	420
	$\eta = 0.025$	-200	380	390	690

a key problem in explaining the complex magnetic properties of these compounds. The interpretation based on the conventional parametrization locating the invisible level near the ground level was originally accepted [36]. The alternative interpretation based on the AOM excludes such a solution definitely if e_σ and e_π were to be positive. Moreover, the new energy level diagram provided by the AOM is consistent with that well known for homologous UCl$_3$ [37]. However, the problem is still far from trivial and requires consistent interpretation of INS and optical spectra, magnetic and relative properties for the whole UX$_3$ series. The recent trial of such interpretation for UCl$_3$ and UBr$_3$ [38] leads to negative AOM parameters again and therefore cannot be accepted.

5. The AOM and Newman's superposition model

It would be of some interest to experimenters interpreting their results in terms of Newman's superposition model (SM) [39] to compare it with the AOM. Both models are founded on the same assumptions and formally, before introducing any assumptions of physico-chemical nature, they are wholly equivalent with the same number of independent parameters. The AOM is based on the parameters e_μ which are equal to change in energy of particular f (in this case) orbitals of axial symmetry μ induced by their interaction with individual ligand t. In the SM [39] the intrinsic parameters $\overline{A}_k$ which are equivalent to the b_ks:

$$\overline{A}_2 = b_2/2 \qquad \overline{A}_4 = b_4/8 \qquad \overline{A}_6 = b_6/16$$

are simply the single-ligand parameters, nothing else. Equations (9) evidence a formal equivalence between the two parametrization schemes for a single-ligand contribution (or group of chemically and crystallographically equivalent ligands). The AOM and SM cease to be equivalent if ligands are not equidistant from the metal ion and the common approximations to the distance dependence of the parameters are introduced: the Newman's power exponent law [39] on the one hand or the square overlap integral scaling of e_μ parameters on the other. Then, contrary to the SM, the $B_{q'}^k/B_q^k$ ratios

provided by the AOM are not completely fixed—they depend to some extent on the value of the e_μ parameters.

In the AOM, apart from the superposition advantage, the commonly powerful chemical concept of the σ, π and δ type bonds is introduced. The definite connection between the parameters e_σ and e_π and the Wolfsberg-Helmholtz formulation of the Hückel molecular orbital model makes the following possible:

(i) theoretical estimation of the distance dependence of the parameters from the proportionality of the metal–ligand interaction to the squares of the appropriate overlap integrals;

(ii) explanation of the problem of the sign of the parameters, it should be definitely positive for donor ligands, negative values are associated with acceptor ligands;

(iii) establishing hierarchy of the parameters: $e_\sigma > e_\pi > |e_\delta|$; and

(iv) prediction or verification of the values of the e_μ parameters on the ground of chemical characteristic of the definite bond only.

The corresponding rules for the parameters $\overline{A}_k$ result from these. Both the revealed hierarchy of the AOM parameters and their distance dependence have their own consequences for them. For example, taking the characteristic relation $e_\pi \simeq e_\sigma/3$ in equation (9) one obtains

$$\overline{A}_2 \simeq \tfrac{15}{28} e_\sigma$$
$$\overline{A}_4 \simeq \tfrac{5}{28} e_\sigma - \tfrac{3}{8} e_\delta \qquad\qquad (27)$$
$$\overline{A}_6 \simeq \tfrac{13}{224} e_\sigma + \tfrac{39}{560} e_\delta.$$

If $e_\delta = 0$ then $\overline{A}_4/\overline{A}_2 \simeq \tfrac{1}{3}$ and $\overline{A}_6/\overline{A}_4 \simeq \tfrac{13}{40}$. In comparison with the results of the SM fittings for the tetravalent actinides U^{4+} and Np^{4+} with Cl^- and O^{2-} ligands [29] the first ratio is too large and the second one too small. As seen from (27), switching on the e_δ parameter changes both ratios in the proper direction.

The intrinsic and universal character of both sets of parameters may be partly lost when the polarization and other mechanisms which are dependent on the entire crystal lattice become important (see section 3.3). In the case of AOM, however, the effect is mainly seen through the e_δ parameter, whereas, as the results obtained with AOM-I indicate, the universal character of the dominating e_σ and e_π parameters is maintained.

Briefly, the parameters provided by the AOM are more natural and fundamental and are better for both their comparison and classification as well as for anticipation of their approximate values if they are unknown.

6. Conclusions

The electronic structure of the actinide ionic systems is successfully tractable within the relatively simple perturbation models. With its background in fundamental quantum-chemical theory the AOM is revealed as a natural consequence of that fact. The modern formulation of the model goes beyond the original concept based on the Wolfsberg-Helmholtz approximation and is open for further generalizations, including breaking down the axial metal–ligand symmetry or non-conventional partitioning of the crystal-field potential.

The thorough discussion of the off-AOM contributions to the crystal-field potential indicates possible limitations to the model. It is shown that its adequacy may become worse when the dominating contributions fulfilling the AOM assumptions are compensated for a given B_q^k due to a specific coordination geometry. Evaluation of the geometrical factors (16) allows one to be prepared for such a case. The important off-AOM contribution characteristic of the actinide systems results from the contact shielding mechanism. Fortunately, its role, from the phenomenological point of view, is limited to low symmetry systems allowing more than one second-order crystal-field parameter.

It should be noted that the phenomenological formula of the AOM is more general than the assumptions which lead to it. Therefore, the validity of the AOM phenomenology is higher than that arising from the traditional definition of the model. This inconsistency may be overcome in a few ways. One of them, perhaps the simplest one, lies in a generalization of the term 'ligand' in the definition.

The *ab initio* calculations show that the original Jørgensen–Schäffer model, referred to here as the AOM-I, is acceptable for the actinide compounds as a first-step approximation and for justifying the square overlap integral scaling of the AOM parameters.

The common AOM version based on both σ and π contributions gains some criticism as being insufficiently accurate. Therefore special attention is paid to the e_δ parameter which is usually neglected. Its inclusion turns out to be advisable in the case of the actinide compounds. It has been shown that it is a lattice-sensitive parameter so there are no hints for predicting its magnitude or even sign besides perhaps its regularity within a homologous and isostructural series.

The dependence of the AOM parameters on the metal–ligand distance is a key problem for coordinations of non-equivalent ligands. For e_σ and e_π it may be easily estimated from the squares of the overlap integrals and approximated by a simple power function. For e_δ such an approximation is acceptable only under certain conditions and should be applied with special caution.

The simplified AOM versions—one-parameter AOM-I and two-parameter AOM-II—find their confirmation in the phenomenological results known for the uranium compounds. It concerns both the predicted ratio of the AOM parameters and their distance dependence. The $e_\sigma(e_\pi)$ parameter provided by the AOM-I fitting may be easily extrapolated from compound to compound and verified according to the spectrochemical ordering of ligands or ionization degree of metals. The AOM-II switching on the e_δ parameter improves the fitting results remarkably. The formal relaxation of the e_π/e_σ ratio, in practice, does not cause any change and has a negligible influence on the results obtained with the AOM-II.

A few examples of the application of the AOM illustrate the promising effectiveness and strength of the AOM phenomenology for the uranium ionic compounds. Numerous examples of the application of the twin SM, available in the literature, may be easily translated into the AOM language to verify them according to the expected regularities of physico-chemical origin and to develop a library of AOM data facilitating subsequent AOM interpretations.

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