

Polynomial approximation of the quantities $\langle r^n \rangle$

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The quantities $\langle r^2 \rangle$ and $\langle r^4 \rangle$ for the elements of the first transition series were calculated. These quantities are important for a quantitative determination of the $d-d$ transitions in coordination compounds. Furthermore, the polynomial approximations of these quantities as functions of the charge on central ion are presented.

В работе сделан расчет величин $\langle r^2 \rangle$ и $\langle r^4 \rangle$ для элементов первой переходной группы. Эти величины важны для количественного определения $d-d$ переходов в координационных соединениях. В работе также приведены полиномы, которые являются приближениями вышеупомянутых величин как функций от заряда на центральном ионе.

In the calculation of electronic structure of coordination compounds by the crystal-field methods we include into the total Hamiltonian the crystal-field operator of the following form

$$\hat{H}_c = \sum_{i=1}^n \hat{V}_i, \quad (1)$$

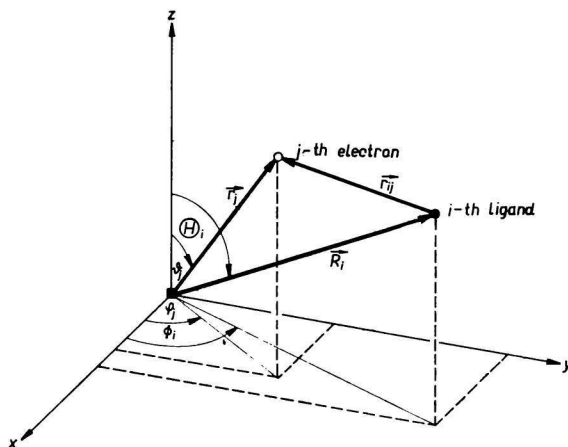


Fig. 1. Coordinate system used.

where

$$\hat{V}_i = \frac{e q_i}{\hat{r}_{ij}}$$

The symbol q_i stands for the charge of the i -th ligand, e is the charge of electron, and \hat{r}_{ij} is the operator of the distance between the i -th ligand and j -th electron of the system (Fig. 1).

The differences between the eigenvalues of the operator \hat{H}_c are relatively large (for the elements of the first transition series 10^3 – 10^4 cm^{-1} ; the multiplets of these elements are of an equal decimal order) so that their omission brings about a considerable distortion of the results of calculation.

It is possible to prove [1–3] that the matrix elements of the operator \hat{H}_c are the subsequent function of the position of ligands

$$\langle k | \hat{H}_c | l \rangle = \sum_{i=1}^N \{ f_1(\Theta_i, \Phi_i) \gamma_6^k \delta_{kl} + f_2(\Theta_i, \Phi_i) \gamma_2^k + f_3(\Theta_i, \Phi_i) \gamma_4^k \}$$

Table 1

Values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ in atomic units for the elements of the first transition series at different degrees of ionization

Ion	$\langle r^2 \rangle$		$\langle r^4 \rangle$	
	1	2	1	2
Ti ⁺	3.507797	3.416773	27.357346	29.570308
Ti ²⁺	2.636622	2.399800	15.442097	12.650874
Ti ³⁺	2.031810	1.910947	9.048803	7.306627
V ²⁺	2.223735	2.027807	11.349818	9.111958
V ³⁺	1.759927	1.632420	6.919091	5.450116
V ⁴⁺	1.445006	1.389133	4.462185	3.752521
Cr ²⁺	1.923359	1.759891	8.642455	7.002609
Cr ³⁺	1.548470	1.435139	5.414418	4.276725
Cr ⁴⁺	1.287828	1.219215	3.575425	2.882740
Mn ²⁺	1.676556	1.528058	6.673119	5.325121
Mn ³⁺	1.372667	1.277690	4.295397	3.425526
Mn ⁴⁺	1.155475	1.102046	2.896634	2.418539
Fe ⁺	1.836036	1.790847	8.358428	8.729728
Fe ²⁺	1.483788	1.390653	5.267749	4.529853
Fe ³⁺	1.223328	1.141402	3.439017	2.764753
Co ⁺	1.609691	1.581726	6.512314	6.750848
Co ²⁺	1.308272	1.261966	4.157789	3.861477
Co ³⁺	1.098347	1.052357	2.788793	2.413926
Ni ⁺	1.425548	1.426581	5.159469	5.751218
Ni ²⁺	1.173795	1.146408	3.362810	3.244621
Ni ³⁺	0.994015	0.965947	2.293021	2.071428
Cu ⁺	1.274006	1.277956	4.148308	4.594757
Cu ²⁺	1.061274	1.043570	2.758662	2.671075

1. Calculated with atomic orbitals according to Richardson *et al.* [4]; 2. calculated with atomic orbitals according to Clementi [5].

where

$$\gamma'_k(R_i) = \frac{e q_i}{R_i^{k+1}} \langle r^k \rangle. \quad (2)$$

(γ_0 is the Madelung potential energy.) The functions $f_i(\Theta_i, \Phi_i)$ are described in the cited papers.

Further we shall concentrate on eqn (2) which determines the magnitude of the splitting of energetic levels for higher degrees of symmetry by means of the radial parameters of crystal-field Dq , Ds , and Dt [1, 2]. For instance, for tetragonal symmetry it holds [2]

$$Dq = \frac{1}{6} \gamma'_4,$$

$$Ds = \frac{2}{7} (\gamma'_2 - \gamma'_4),$$

$$Dt = \frac{2}{21} (\gamma'_4 - \gamma'_2),$$

where γ'_k and γ''_k are equatorial and axial quantities, respectively.

Table 2

Approximating polynomials of the quantities $\langle r^2 \rangle$ and $\langle r^4 \rangle$ for the elements of the first transition series

	$\langle r^n \rangle_{\text{approx.}} = \sum_{j=0}^m a_j Q^{m-j}$	$\Delta \cdot 10^6$	Atomic orbitals
Ti	$r^2 = -0.03224746 Q^3 + 0.32666621 Q^2 - 1.62544126 Q + 4.83881931$	0.19	1
	$r^2 = 0.26405993 Q^2 - 1.80915281 Q + 4.96186581$	0.03	2
	$r^4 = -1.09355594 Q^3 + 9.32230529 Q^2 - 32.22726309 Q + 51.35585439$	5.66	1
	$r^4 = 5.78759165 Q^2 - 34.28220701 Q + 58.06492245$	1.34	2
V	$r^2 = 0.00035970 Q^4 - 0.01889854 Q^3 + 0.22474686 Q^2 - 1.25185006 Q + 3.97388055$	0.52	1
	$r^2 = -0.03187660 Q^3 + 0.36293888 Q^2 - 1.60442562 Q + 4.03991513$	0.35	2
	$r^4 = 0.08201377 Q^4 - 1.15205937 Q^3 + 6.84467454 Q^2 - 22.09585047 Q + 36.06706619$	8.85	1
	$r^4 = -0.80556543 Q^3 + 8.23221087 Q^2 - 29.517150 Q + 41.66193545$	2.95	2
Cr	$r^2 = -0.00015218 Q^5 + 0.00337079 Q^4 - 0.03347934 Q^3 + 0.21640767 Q^2 - 1.00780216 Q + 3.29210023$	4.40	1
	$r^2 = 0.00225171 Q^4 - 0.03692948 Q^3 + 0.26292187 Q^2 - 1.08404860 Q + 3.13570371$	8.02	2
	$r^4 = -0.00698692 Q^5 + 0.13152564 Q^4 - 1.06938703 Q^3 + 5.07612672 Q^2 - 15.36496234 Q + 25.74199748$	142.63	1
	$r^4 = 0.06444552 Q^4 - 1.00307022 Q^3 + 6.14870988 Q^2 - 18.59967285 Q + 26.60038424$	220.69	2

Table 2 (Continued)

	$\langle r^n \rangle_{\text{approx.}} = \sum_{j=0}^m a_j Q^{m-j}$	$\Delta \cdot 10^6$	Atomic orbitals
Mn	$r^2 = 0.00012055 Q^5 - 0.00056932 Q^4 - 0.01096040 Q^3 + 0.13894349 Q^2 - 0.77878207 Q + 2.77127782$	3.10	1
	$r^2 = -0.00072375 Q^5 + 0.01649678 Q^4 - 0.14706427 Q^3 + 0.66054658 Q^2 - 1.67906116 Q + 3.17993725$	383.18	2
	$r^4 = -0.00352203 Q^5 + 0.07257777 Q^4 - 0.64501290 Q^3 + 3.30643649 Q^2 - 10.62888199 Q + 18.81660706$	94.16	1
	$r^4 = -0.01406928 Q^5 + 0.30607930 Q^4 - 2.62478335 Q^3 + 11.25571767 Q^2 - 25.24383992 Q + 27.34478199$	6366.84	2
Fe	$r^2 = -0.00073980 Q^5 + 0.01019033 Q^4 - 0.05585370 Q^3 + 0.19284548 Q^2 - 0.66973402 Q + 2.35932868$	3.93	1
	$r^2 = 0.00070950 Q^5 - 0.01154153 Q^4 + 0.06118783 Q^3 - 0.06683762 Q^2 - 0.47695115 Q + 2.28429563$	117.68	2
	$r^4 = -0.00538656 Q^5 + 0.08680781 Q^4 - 0.60189464 Q^3 + 2.55704893 Q^2 - 7.68379349 Q + 14.00567749$	64.34	1
	$r^4 = -0.00051723 Q^5 + 0.03694528 Q^4 - 0.57424988 Q^3 + 3.78412100 Q^2 - 12.06959596 Q + 17.55283326$	1484.89	2
Co	$r^2 = 0.00015248 Q^5 - 0.00163202 Q^4 + 0.00054269 Q^3 + 0.06956788 Q^2 - 0.49416814 Q + 2.03522819$	0.29	1
	$r^2 = -0.00058973 Q^5 + 0.01059188 Q^4 - 0.07577544 Q^3 + 0.29776317 Q^2 - 0.82306829 Q + 2.17277652$	215.98	2
	$r^4 = -0.00101746 Q^5 + 0.02411383 Q^4 - 0.25017029 Q^3 + 1.48258146 Q^2 - 5.38130392 Q + 10.63813052$	40.01	1
	$r^4 = -0.00289432 Q^5 + 0.06073425 Q^4 - 0.54289890 Q^3 + 2.71875305 Q^2 - 8.06559220 Q + 12.58255470$	1485.44	2
Ni	$r^2 = -0.00011631 Q^5 + 0.00168337 Q^4 - 0.01306312 Q^3 + 0.08275400 Q^2 - 0.43022190 Q + 1.78451322$	2.910	1
	$r^2 = 0.00010705 Q^5 - 0.00081152 Q^4 - 0.00647906 Q^3 + 0.09933480 Q^2 - 0.52394010 Q + 1.85836434$	43.78	2
	$r^4 = -0.00138404 Q^5 + 0.02560166 Q^4 - 0.21847681 Q^3 + 1.15887583 Q^2 - 4.08511947 Q + 8.27998936$	33.33	1
	$r^4 = -0.00100893 Q^5 + 0.03246482 Q^4 - 0.38617575 Q^3 + 2.26179259 Q^2 - 7.04373331 Q + 10.88774815$	1012.18	2
Cu	$r^2 = -0.00029606 Q^5 + 0.00428817 Q^4 - 0.02530354 Q^3 + 0.0981793 Q^2 - 0.38529429 Q + 1.58243398$	2.85	1
	$r^2 = -0.00013844 Q^5 + 0.00296377 Q^4 - 0.02692029 Q^3 + 0.13997789 Q^2 - 0.50598459 Q + 1.66804749$	84.28	2
	$r^4 = -0.0020312 Q^5 + 0.03293373 Q^4 - 0.22999952 Q^3 + 1.00293371 Q^2 - 3.21952239 Q + 6.56400439$	22.65	1
	$r^4 = -0.00405618 Q^5 + 0.08298278 Q^4 - 0.68030718 Q^3 + 2.89439293 Q^2 - 6.96249944 Q + 9.26401961$	1730.96	2

The quantities in expression (2) being known (except q_i which may be a parameter of the problem solved), we have to determine only the quantity $\langle r^k \rangle$ (where $k=2, 4$ because $\langle r^0 \rangle = 1$). This quantity is defined by the relation

$$\langle r^k \rangle_{\text{calc}} = \int_0^\infty R_{3d}^2(r) r^{k+2} dr.$$

Provided a good set of radial atomic orbitals $R_{3d}(r)$ for different degrees of ionization of the central ion, then this quantity may be regarded as a function of particular degrees of ionization. Such sets of atomic orbitals were described by *Richardson, Nieuwpoort, Powell, and Edgell* [4], *Clementi* [5], and *Watson* [6].

The calculated values of the quantities $\langle r^2 \rangle$ and $\langle r^4 \rangle$ for the most usual ionization degrees of elements of the first transition series are given in Table 1. These quantities were calculated by using the atomic orbitals according to [4, 5]. (The author did not have at his disposal the atomic orbitals according to Watson.)

Smith [7] takes into consideration the possibility of a non-integer degree of ionization (charge on central atom), *i.e.* the function

$$\langle r^k \rangle_{\text{approx.}} = f(Q), \quad (3)$$

where Q is a non-integer charge on the central ion.

For a sufficiently high number $\langle r^k \rangle_{\text{calc}}$ functional relationship (3) may be approximated, *e.g.* by a polynomial of higher order of the form

$$\langle r^k \rangle_{\text{approx.}} = \sum_{j=0}^m a_j Q^{m-j}, \quad (4)$$

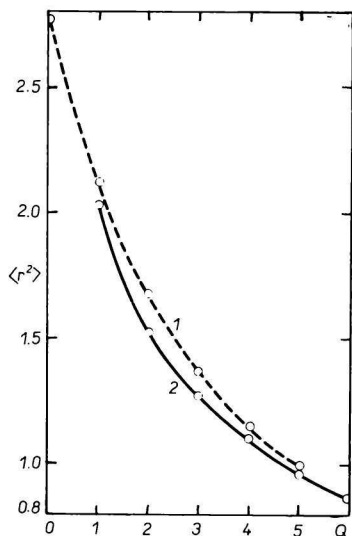


Fig. 2. $\langle r^2 \rangle$ vs. Q curve.

1. Calculated with atomic orbitals according to *Richardson et al.* [4]; 2. calculated with atomic orbitals according to *Clementi* [5].

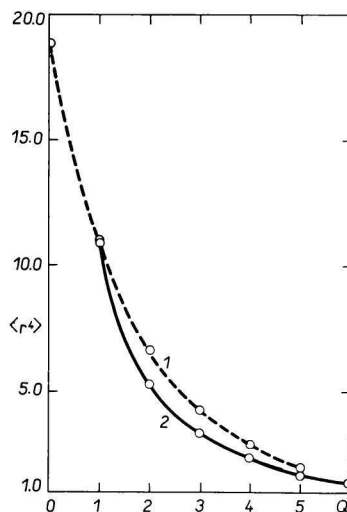


Fig. 3. $\langle r^4 \rangle$ vs. Q curve.

1. Calculated with atomic orbitals according to *Richardson et al.* [4]; 2. calculated with atomic orbitals according to *Clementi* [5].

where m is the degree of the polynomial.

These polynomials for the elements of the first transition series as well as the maximum deviations of individual polynomials from $\langle r^k \rangle_{\text{calc}}$ are given in Table 2. The quantity Δ is defined by the relationship

$$\Delta = |\langle r^k \rangle_{\text{calc}} - \langle r^k \rangle_{\text{approx.}}|.$$

The expansion coefficients a_i in relationship (4) were calculated by the method of least squares [8].

The $\langle r^k \rangle$ — Q curves of the element Mn calculated by using the mentioned atomic orbitals for $k=2, 4$ are shown in Figs. 2 and 3. For all elements of the first transition series the character of the $\langle r^k \rangle$ — Q curves is similar to that of the curves in Figs. 2 and 3.

The programs were written in both FORTRAN and ALGOL languages and may be given on request to all interested in this problem.

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