

THE EFFECTIVE CRYSTAL FIELD POTENTIAL

JACEK MULAŁ and ZBIGNIEW GAJEK

*W. Trzebiatowski Institute of Low Temperature and
Structure Research, Polish Academy of Sciences,
Wrocław, Poland*

2000



ELSEVIER

Amsterdam - Lausanne - New York - Oxford - Shannon - Singapore - Tokyo

CONTENTS

1. Introduction	1
2. Parameterization of crystal field Hamiltonian	11
2.1. Operators and parameters of the crystal field Hamiltonian	12
2.1.1. Operators related to spherical harmonics	13
2.1.2. Operators related to tesseral harmonics	13
2.2. Basic parameterizations	14
2.2.1. $C_q^{(k)}$ tensor operator parameterization	14
2.2.2. O_k^q Stevens operator equivalent method	16
2.3. Symmetry transformations of the operators	18
2.4. The number of independent crystal field parameters	23
2.5. Standardization of the crystal field Hamiltonian	26
2.6. Final remark	29
3. The effective crystal field potential.	
Chronological development of crystal field models	31
4. Ionic complex or quasi-molecular cluster.	
Generalized product function	41
4.1 Concept of the generalized product function	41
4.2 The density functions and the transition density functions	43
4.3 Model of the generalized product functions	44
4.4 Crystal field effect in the product function model	49
5. Point charge model (PCM)	53
5.1 PCM potential and its parameters	53
5.2 Simple partial PCM potentials	56
5.3 Extension of PCM – higher point multipole contribution	61
6. One-configurational model with neglecting the non-orthogonality. The charge penetration and exchange effects	65
6.1 Classical electrostatic potential produced by the ligand charge distribution	65
6.2 The charge penetration effect and the exchange interaction in the generalized product function model	68
6.3 The weight of the penetration and exchange effects in the crystal field potential	71
6.4 Calculation of the two-centre integrals	73
6.5 Final remarks	74

7. The exclusion model. One-configurational approach with regard to non-orthogonality of the wave functions	77
7.1 Three types of the non-orthogonality	77
7.2 The renormalization of the open-shell Hamiltonian H_a owing to the non-orthogonality of the one-electron functions	79
7.3 The contact-covalency – the main component of the crystal field potential	84
7.4 The contact-shielding	87
7.5 The contact-polarization	88
7.6 Mechanisms of the contact-shielding and contact-polarization in terms of the exchange charge notion	88
8. Covalency contribution, i.e. the charge transfer effect	91
8.1 The one-electron excitations. Group product function for the excited state	91
8.2 The renormalization of the open-shell Hamiltonian due to the covalency effect	94
8.3 Basic approximations	96
8.4 The one-electron covalency potential V^{cov}	97
8.5 The one-electron covalency potential V^{cov} in the molecular-orbital formalism	101
8.6 Remarks on the covalency mechanism	102
9. Shielding and antishielding effect: contributions from closed electron shells	105
9.1 Phenomenological quantification of the screening effect	106
9.2 Microscopic model of the screening effect	107
9.3 General expressions for the screening factors	109
9.4 The screening factors	116
10. Electrostatic crystal field contributions with consistent multipolar effects. Polarization	119
10.1 Expansion of the electrostatic potential of point charge system into the multipole series	119
10.2 Extended formula for the crystal field parameters including all multipole moments of the surroundings	121
10.3 The self-consistent system of permanent and induced multipole moments in crystal lattice	126
10.4 The off-axial polarization terms in local coordinate systems	127
10.5 Typical examples of dipole and quadrupole polarization contributions to the crystal field potential	129

11. Crystal field effect in the Stevens perturbation approach	131
11.1 The Wannier functions	132
11.2 The perturbation scheme for degenerate systems employing projection operators	133
11.3 The crystal field effect	136
12. Specific mechanisms of metallic states contributing to the crystal field potential	143
13. Screening the crystal field in metallic materials	147
13.1 The Fourier form of the crystal lattice potential	149
13.2 The dielectric static screening function $\epsilon(\mathbf{q})$	153
13.3 The dynamic mechanism of the screening - zero-point plasmon	159
14. Virtual bound state contribution to the crystal field potential	163
14.1 The resonance scattering of conduction electrons by a central potential	163
14.2 The nature of the virtual bound state	166
14.3 Spin-polarization of the virtual bound state	167
14.4 Experimental manifestations of existing the virtual bound states and methods of estimating their localization degree	167
14.5 The crystal field splitting of the virtual bound state	168
14.6 The primary crystal field effect relative to the open-shell states (4f)	169
14.7 Corrections to the simple model of the virtual bound state mechanism	174
15. Hybridization or covalent mixing between localized states and conduction band states in metallic crystals	177
15.1 The essence of the hybridization	177
15.2 Hybridization contribution to the crystal field parameters	178
15.3 The scale of the hybridization effect	182
15.4 Contribution to the crystal field potential from a split-off state from the conduction band in impurity systems	184

16. Density functional theory approach	185
16.1 Electron density as a key variable	185
16.2 The Kohn–Sham equations	188
16.3 Local density approximation	190
16.4 Extensions	192
16.4.1 Degenerate ground state and excited states	192
16.4.2 Multicomponent system	196
16.4.3 Local spin density approximation	197
16.4.4 Relativistic effects	198
16.5 Exchange-correlation energy	201
16.5.1 Self-interaction correction	201
16.5.2 Generalized gradient approximation	203
16.6 Mapping DFT on effective Hamiltonian	204
16.7 Applications	206
16.7.1 Ionic compounds	206
16.7.2 Intermetallic compounds	207
16.7.3 Final remarks	208
17. Analysis of the experimental data. Interpretation of crystal field parameters with additive models	211
17.1 Phenomenological Hamiltonian	212
17.2 Simplified crystal field models	215
17.2.1 Decomposition of the CF potential. Virtual ligands	216
17.2.2 Superposition model and angular overlap model	218
17.2.3 Limitations	221
17.2.4 Non-equivalent ligands	223
17.3 Towards applications	224
18. Lattice dynamics contribution	229
18.1 Adiabatic and harmonic approximations	230
18.2 Collective (normal) coordinates and the "quasi-molecular" model	233
18.3 The Jahn-Teller effect	235
18.4 Lattice dynamics and the crystal field effect	241
19. Extension of the crystal field potential beyond the one-electron model	247
19.1 Two-electron correlation effect in the crystal field model	247
19.2 Parameterization of the two-electron potential	248
19.3 The term dependent crystal field	250
19.4 Spin correlated crystal field (SCCF)	252
19.5 Many-electron approach to the crystal field effect	254

20. Appendices	257
A. Transformation from local to the global coordinate system	257
B. $3n$ -j symbols	259
C. Methods of orthogonalization of functions	261
21. References	263
22. Author index	287
23. Subject index	293