

2. SYMMETRY ASPECTS OF EXCITATIONS

 Table 2.2.16.1. $W_{\ell\ell'}$ factors for X-ray emission spectra showing the $\Delta\ell = \pm 1$ selection rule

ℓ'	ℓ				
	0	1	2	3	4
0					
1	1	1/3	2/5		
2		2/3		3/7	
3			3/5		4/11

2.2.16.3. Core electron spectra

In excitations involving core electrons, simplifications are possible that allow an easier interpretation. As one example, (soft) X-ray emission (XES) or absorption (XAS) spectra are briefly discussed. In the one-electron picture, the XES process can be described as sketched in Fig. 2.2.16.4. First a core electron of atom A in state $n'\ell'$ is knocked out (by electrons or photons), and then a transition occurs between the occupied valence states at energy ε and the core hole (the transitions between inner core levels are ignored).

According to Fermi's golden rule, the intensity of such a transition can be described by

$$I_{An'\ell'}(\nu) = \nu^3 \sum_{\ell} W_{\ell\ell'} n_{\ell}^A(\varepsilon) M_A(\ell, n'\ell', \varepsilon)^2 \delta(\varepsilon - E_{n'\ell'}^A - h\nu), \quad (2.2.16.5)$$

where $W_{\ell\ell'}$ comes from the integral over the angular components (Table 2.2.16.1) and contains the $\Delta\ell = \pm 1$ selection rule, $n_{\ell}^A(\varepsilon)$ is the local (within atomic sphere A) partial (ℓ -like) DOS, $M_A(\ell, n'\ell', \varepsilon)^2$ is the radial transition probability [see (2.2.16.6) below], and the last term takes the energy conservation into account.

The $M_A(\ell, n'\ell', \varepsilon)^2$ are defined as the dipole transition (with the dipole operator r) probability between the valence state at ε and the core state characterized by quantum numbers $n'\ell'$,

$$M_A(\ell, n'\ell', \varepsilon)^2 = \frac{[\int_0^{R_A} u_{\ell}^A(r, \varepsilon) r^3 R_{n'\ell'}^{A \text{ core}}(r) dr]^2}{\int_0^{R_A} [u_{\ell}^A(r, \varepsilon)]^2 r^2 dr}. \quad (2.2.16.6)$$

In this derivation one makes use of the fact that core states are completely confined inside the atomic sphere. Therefore the integral, which should be taken over the entire space, can be restricted to one atomic sphere (namely A), since the core wavefunction $R_{n'\ell'}^{A \text{ core}}(r)$ and thus the integrand vanishes outside this sphere. This is also the reason why XES (or XAS) are related to $n_{\ell}^A(\varepsilon)$, the local DOS weighted with the ℓ -like charge within the atomic sphere A .

The interpretation of XES intensities is as follows. Besides the ν^3 factor from Fermi's golden rule, the intensity is governed by the $\Delta\ell = \pm 1$ selection rule and the energy conservation. In addition, it depends on the number of available states at ε which reside inside sphere A and have an ℓ -like contribution, times the probability for the transition to take place from the valence and to the core hole under energy conservation. For an application, see for example the comparison between theory and experiment for the compounds NbC and NbN (Schwarz, 1977).

Note again that the present description is based on an atomic sphere representation with partial waves inside the spheres, in contrast to an LCAO-like treatment with site-centred basis functions. In the latter, an equivalent formalism can be defined which differs in details, especially for the small components (off-site contributions). If the tails of an orbital enter a neighbouring sphere and are crucial for the interpretation of XES, there is a semantic difference between the two schemes as discussed above in connection with f.c.c. Cu in Section 2.2.16.1. In the present framework, all contributions come exclusively from the sphere where the core hole resides, whereas in an LCAO representation 'cross transitions' from the valence states on one atom to the core

hole of a neighbouring atom may be important. The latter contributions must be (and are) included in the partial waves within the sphere in schemes such as LAPW. There is no physical difference between the two descriptions.

In XES, spectra are interpreted on the basis of results from ground-state calculations, although there could be relaxations due to the presence of a core hole. As early as 1979, von Barth and Grossmann formulated a 'final state rule' for XES in metallic systems (von Barth & Grossmann, 1979). In this case, the initial state is one with a missing core electron (core hole), whereas the final state is close to the ground state, since the hole in the valence bands (after a valence electron has filled the core hole) has a very short lifetime and is very quickly filled by other valence electrons. They applied time-dependent perturbation theory and could show by model calculations that the main XES spectrum can be explained by ground-state results, whereas the satellite spectrum (starting with two core holes and ending with one) requires a treatment of the core-hole relaxation. This example illustrates the importance of the relevant physical process in experiments related to the energy-band structure: it may not always be the just the ground states that are involved and sometimes excited states must be considered.

2.2.17. Conclusion

There are many more applications of band theory to solids and thus an enormous amount of literature has not been covered here. In this chapter, an attempt has been made to collect relevant concepts, definitions and examples from group theory, solid-state physics and crystallography in order to understand symmetry aspects in combination with a quantum-mechanical treatment of the electronic structure of solids.

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References

- Akai, H., Akai, M., Blügel, S., Drittler, B., Ebert, H., Terakura, K., Zeller, R. & Dederichs, P. H. (1990). *Theory of hyperfine interactions in metals*. *Prog. Theor. Phys. Suppl.* **101**, 11–77.
- Altmann, S. L. (1994). *Band theory of solids: An introduction from the view of symmetry*. Oxford: Clarendon Press.
- Andersen, O. K. (1975). *Linear methods in band theory*. *Phys. Rev. B*, **12**, 3060–3083.
- Barth, U. von & Grossmann, G. (1979). *The effect of the core hole on X-ray emission spectra in simple metals*. *Solid State Commun.* **32**, 645–649.
- Barth, U. von & Hedin, L. (1972). *A local exchange-correlation potential for the spin-polarized case: I*. *J. Phys. C*, **5**, 1629–1642.
- Blaha, P., Schwarz, K. & Dederichs, P. H. (1988). *First-principles calculation of the electric field gradient in hcp metals*. *Phys. Rev. B*, **37**, 2792–2796.
- Blaha, P., Schwarz, K. & Herzig, P. (1985). *First-principles calculation of the electric field gradient of Li_3N* . *Phys. Rev. Lett.* **54**, 1192–1195.
- Blaha, P., Schwarz, K., Sorantin, P. I. & Trickey, S. B. (1990). *Full-potential linearized augmented plane wave programs for crystalline systems*. *Comput. Phys. Commun.* **59**, 399–415.
- Blaha, P., Singh, D. J., Sorantin, P. I. & Schwarz, K. (1992). *Electric field gradient calculations for systems with large extended core state contributions*. *Phys. Rev. B*, **46**, 5849–5852.
- Blöchl, P. E. (1994). *Projector augmented-wave method*. *Phys. Rev. B*, **50**, 17953–17979.
- Bouckaert, L. P., Smoluchowski, R. & Wigner, E. (1930). *Theory of Brillouin zones and symmetry properties of wavefunctions in crystals*. *Phys. Rev.* **50**, 58–67.
- Bradley, C. J. & Cracknell, A. P. (1972). *The mathematical theory of symmetry in solids*. Oxford: Clarendon Press.

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- Car, R. & Parrinello, M. (1985). *Unified approach for molecular dynamics and density-functional theory*. *Phys. Rev. Lett.* **55**, 2471–2474.
- Ceperley, D. M. & Alder, B. J. (1984). *Ground state of the electron gas by a stochastic method*. *Phys. Rev. Lett.* **45**, 566–572.
- Colle, R. & Salvetti, O. (1990). *Generalisation of the Colle–Salvetti correlation energy method to a many determinant wavefunction*. *J. Chem. Phys.* **93**, 534–544.
- Condon, E. U. & Shortley, G. H. (1953). *The mathematical theory of symmetry in crystals*. Cambridge University Press.
- Dreizler, R. M. & Gross, E. K. U. (1990). *Density functional theory*. Berlin, Heidelberg, New York: Springer-Verlag.
- Dufek, P., Blaha, P. & Schwarz, K. (1995a). *Theoretical investigation of the pressure induced metallization and the collapse of the antiferromagnetic states in NiI₂*. *Phys. Rev. B*, **51**, 4122–4127.
- Dufek, P., Blaha, P. & Schwarz, K. (1995b). *Determination of the nuclear quadrupole moment of ⁵⁷Fe*. *Phys. Rev. Lett.* **75**, 3545–3548.
- Ellis, D. E., Guenzburger, D. & Jansen, H. B. (1983). *Electric field gradient and electronic structure of linear-bonded halide compounds*. *Phys. Rev. B*, **28**, 3697–3705.
- Godby, R. W., Schlüter, M. & Sham, L. J. (1986). *Accurate exchange-correlation potential for silicon and its discontinuity of addition of an electron*. *Phys. Rev. Lett.* **56**, 2415–2418.
- Gunnarsson, O. & Lundqvist, B. I. (1976). *Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formation*. *Phys. Rev. B*, **13**, 4274–4298.
- Hedin, L. & Lundqvist, B. I. (1971). *Explicit local exchange-correlation potentials*. *J. Phys. C*, **4**, 2064–2083.
- Herzig, P. (1985). *Electrostatic potentials, field gradients from a general crystalline charge density*. *Theoret. Chim. Acta*, **67**, 323–333.
- Hoffmann, R. (1988). *Solids and surfaces: A chemist's view of bonding in extended structures*. New York: VCH Publishers, Inc.
- Hohenberg, P. & Kohn, W. (1964). *Inhomogeneous electron gas*. *Phys. Rev.* **136**, B864–B871.
- Hybertsen, M. S. & Louie, G. (1984). *Non-local density functional theory for the electronic and structural properties of semiconductors*. *Solid State Commun.* **51**, 451–454.
- International Tables for Crystallography* (2000). Vol. B. *Reciprocal space*, edited by U. Shmueli, 2nd ed. Dordrecht: Kluwer Academic Publishers.
- International Tables for Crystallography* (2002). Vol. A. *Space-group symmetry*, edited by Th. Hahn, 5th ed. Dordrecht: Kluwer Academic Publishers.
- Janak, J. F. (1978). *Proof that $\partial E/\partial n_i = \epsilon_i$ in density-functional theory*. *Phys. Rev. B*, **18**, 7165–7168.
- Kaufmann, E. N. & Vianden, R. J. (1979). *The electric field gradient in noncubic metals*. *Rev. Mod. Phys.* **51**, 161–214.
- Koelling, D. D. & Arbmán, G. O. (1975). *Use of energy derivative of the radial solution in an augmented plane wave method: application to copper*. *J. Phys. F Metal Phys.* **5**, 2041–2054.
- Koelling, D. D. & Harmon, B. N. (1977). *A technique for relativistic spin-polarized calculations*. *J. Phys. C Solid State Phys.* **10**, 3107–3114.
- Kohn, W. & Rostocker, N. (1954). *Solution of the Schrödinger equation in periodic lattice with an application to metallic lithium*. *Phys. Rev.* **94**, A1111–A1120.
- Kohn, W. & Sham, L. J. (1965). *Self-consistent equations including exchange*. *Phys. Rev.* **140**, A1133–A1138.
- Korringa, J. (1947). *On the calculation of the energy of a Bloch wave in a metal*. *Physica*, **13**, 392–400.
- Kurki-Suonio, K. (1977). *Symmetry and its implications*. *Isr. J. Chem.* **16**, 115–123.
- Loucks, T. L. (1967). *Augmented plane wave method*. New York, Amsterdam: W. A. Benjamin, Inc.
- Methfessel, M. & Frota-Pessoa, S. (1990). *Real-space method for calculation of the electric-field gradient: Comparison with K-space results*. *J. Phys. Condens. Matter*, **2**, 149–158.
- Meyer, B., Hummler, K., Elsässer, C. & Fähnle, M. (1995). *Reconstruction of the true wavefunction from the pseudo-wavefunctions in a crystal and calculation of electric field gradients*. *J. Phys. Condens. Matter*, **7**, 9201–9218.
- Ordejon, P., Drabold, D. A., Martin, R. A. & Grumbach, M. P. (1995). *Linear system-size scaling methods for electronic-structure calculations*. *Phys. Rev. B*, **51**, 1456–1476.
- Parr, R., Donnelly, R. A., Levy, M. & Palke, W. A. (1978). *Electronegativity: the density functional viewpoint*. *J. Chem. Phys.* **68**, 3801–3807.
- Perdew, J. P. (1986). *Density functional theory and the band gap problem*. *Int. J. Quantum Chem.* **19**, 497–523.
- Perdew, J. P., Burke, K. & Ernzerhof, M. (1996). *Generalized gradient approximation made simple*. *Phys. Rev. Lett.* **77**, 3865–3868.
- Perdew, J. P. & Levy, M. (1983). *Physical content of the exact Kohn–Sham orbital energies: band gaps and derivative discontinuities*. *Phys. Rev. Lett.* **51**, 1884–1887.
- Petrilli, H. M., Blöchl, P. E., Blaha, P. & Schwarz, K. (1998). *Electric-field-gradient calculations using the projector augmented wave method*. *Phys. Rev. B*, **57**, 14690–14697.
- Petrilli, H. M. & Frota-Pessoa, S. (1990). *Real-space method for calculation of the electric field gradient in systems without symmetry*. *J. Phys. Condens. Matter*, **2**, 135–147.
- Pisani, C. (1996). *Quantum-mechanical ab-initio calculation of properties of crystalline materials. Lecture notes in chemistry*, **67**, 1–327. Berlin, Heidelberg, New York: Springer-Verlag.
- Pyykkö, P. (1992). *The nuclear quadrupole moments of the 20 first elements: High-precision calculations on atoms and small molecules*. *Z. Naturforsch. A*, **47**, 189–196.
- Sandratskii, L. M. (1990). *Symmetry properties of electronic states of crystals with spiral magnetic order*. *Solid State Commun.* **75**, 527–529.
- Schwarz, K. (1977). *The electronic structure of NbC and NbN*. *J. Phys. C Solid State Phys.* **10**, 195–210.
- Schwarz, K., Ambrosch-Draxl, C. & Blaha, P. (1990). *Charge distribution and electric field gradients in YBa₂Cu₃O_{7-x}*. *Phys. Rev. B*, **42**, 2051–2061.
- Schwarz, K. & Blaha, P. (1992). *Ab initio calculations of the electric field gradients in solids in relation to the charge distribution*. *Z. Naturforsch. A*, **47**, 197–202.
- Schwarz, K. & Blaha, P. (1996). *Description of an LAPW DF program (WIEN95)*. In *Lecture notes in chemistry*, Vol. 67, *Quantum-mechanical ab initio calculation of properties of crystalline materials*, edited by C. Pisani. Berlin, Heidelberg, New York: Springer-Verlag.
- Schwarz, K. & Herzig, P. (1979). *The sensitivity of partially filled f bands to configuration and relativistic effects*. *J. Phys. C Solid State Phys.* **12**, 2277–2288.
- Seitz, F. (1937). *On the reduction of space groups*. *Ann. Math.* **37**, 17–28.
- Singh, D. J. (1994). *Plane waves, pseudopotentials and the LAPW method*. Boston, Dordrecht, London: Kluwer Academic Publishers.
- Skriver, H. L. (1984). *The LMTO method. Springer series in solid-state sciences*, Vol. 41. Berlin, Heidelberg, New York, Tokyo: Springer.
- Slater, J. C. (1937). *Wavefunctions in a periodic crystal*. *Phys. Rev.* **51**, 846–851.
- Slater, J. C. (1974). *The self-consistent field for molecules and solids*. New York: McGraw-Hill.
- Sorantin, P. & Schwarz, K. (1992). *Chemical bonding in rutile-type compounds*. *Inorg. Chem.* **31**, 567–576.
- Springborg, M. (1997). *Density-functional methods in chemistry and material science*. Chichester, New York, Weinheim, Brisbane, Singapore, Toronto: John Wiley and Sons Ltd.
- Vosko, S. H., Wilk, L. & Nusair, M. (1980). *Accurate spin-dependent electron liquid correlation energies for local spin density calculations*. *Can. J. Phys.* **58**, 1200–1211.
- Weinert, M. (1981). *Solution of Poisson's equation: beyond Ewald-type methods*. *J. Math. Phys.* **22**, 2433–2439.
- Williams, A. R., Kübler, J. & Gelatt, C. D. Jr (1979). *Cohesive properties of metallic compounds: Augmented-spherical-wave calculations*. *Phys. Rev. B*, **19**, 6094–6118.
- Winkler, B., Blaha, P. & Schwarz, K. (1996). *Ab initio calculation of electric field gradient tensors of fosterite*. *Am. Mineral.* **81**, 545–549.