lattice). *It is important to record that the crystal field theory considers the ligand atoms as point charges or point dipoles, and does not consider any overlap between ligand orbitals and metal ion orbitals*. Crystal field theory examines the energetics of the *d*-orbitals, in particular, in given geometries.

The five d-orbitals are degenerate in a field-free ion. The five d-orbitals are not all alike. The three orbitals d_{xy}, d_{xz}, d_{yz} have their four lobes concentrated in between the coordinate axes : for example d_{xy} orbital has its four lobes between the x and y axes. The $d_{x^2-y^2}$ orbital has its lobes along the x and the y axes. The d_{z^2} orbital has two lobes along the *z-axis* and a concentric lobe all around the nucleus in the xy plane. When such a set of five d-orbitals is subjected to an octahedral crystal field the d-orbitals can no longer remain degenerate. Their overall energy is raised from that in the absence of any field, and they undergo splitting. Since the $d_{x^2-y^2}$ and the d_{z^2} orbitals are face to face with the six ligands they are now raised in energy whereas the d_{xy}, d_{xz}, d_{yz} orbitals are lowered in energy. The splitting is so adjusted that the centre of gravity (baricentre) of the five degenerate d-orbitals in a uniformly smeared out field of six negative charges is maintained (Fig. 10.7). The difference in energy of the orbitals d_{xy}, d_{xz}, d_{yz} (t_{2g} set) and the $d_{x^2-y^2}$, d_{z^2} orbitals (e_g set) is given as symbol Δ or 10 *Dq*, this difference being a measure of the strength of the crystal field operating on the metal ion. Δ or 10 *Dq*, is the separation between the $t_{2g}(d_{xy})$ and the e_g $(d_{x^2-y^2})$ and is known as the *crystal field splitting parameter* or as the *crystal field strength.*

Since the pre-splitting centre of gravity is to be maintained the e_g set will go up by say x and the t_{2g} set will go down by say y. If E is the energy of each electron prior to splitting it follows that :

$$10E = 4(E + x) + 6\,(E - y) \text{ so that } 2x = 3y$$

Also since $x + y = \Delta$ we have $x = \frac{3}{5}\Delta = 6\,Dq$ and $y = \frac{2}{5}\Delta = 4\,Dq$. Thus each t_{2g} electron is stabilised by $-4Dq$ and each e_g electron is destabilised by $+ 6\,Dq$. with respect to the unsplit baricentre energy.

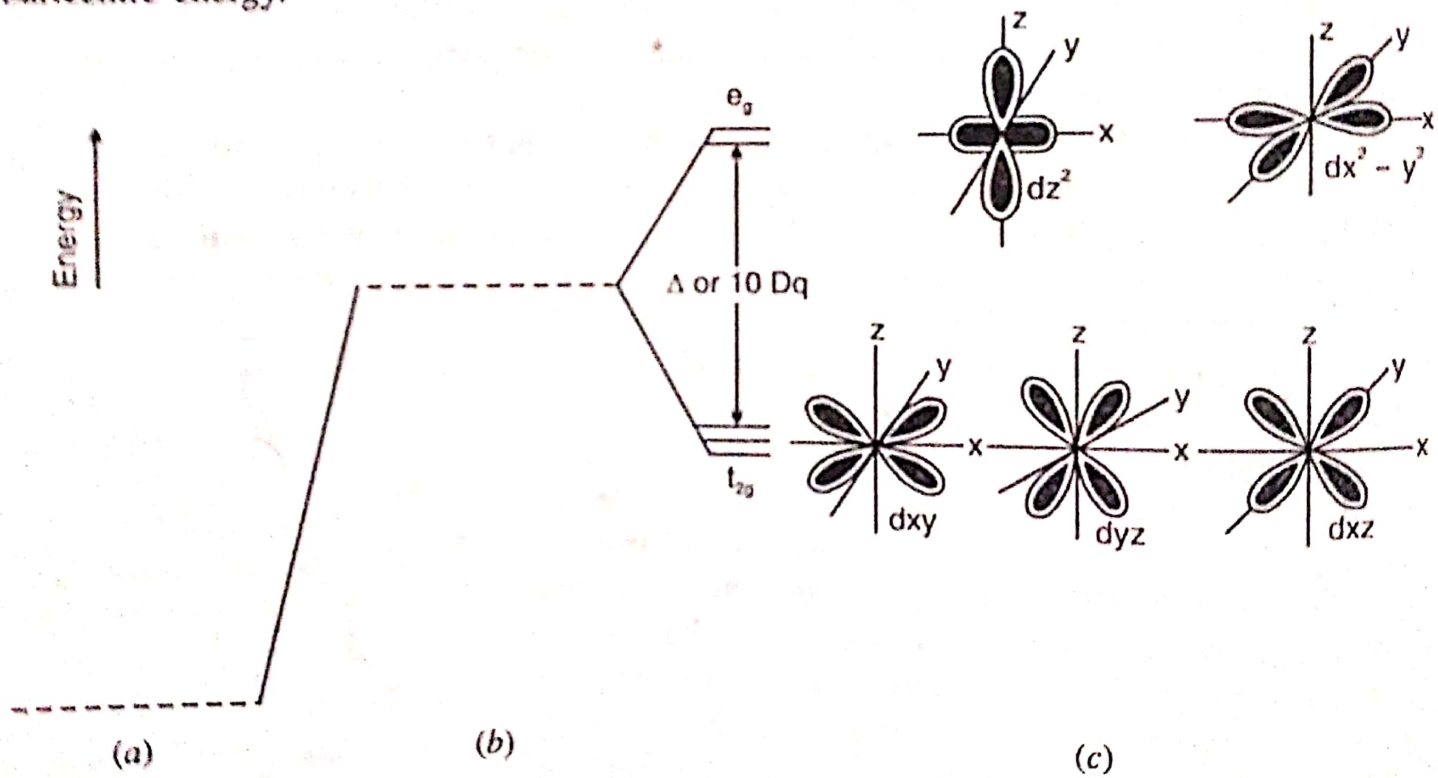

Fig. 10.7. Splitting of the d-orbitals in an octahedral field. (a) free ion (b) smeared out field (c) splitting

The symbol t_{2g} indicates a *triplet orbital degenearcy* i.e. a three fold degeneracy comprising *in this case* the orbitals d_{xy}, d_{xz}, d_{yz}. The symbol e speaks of a *two fold degeneracy* comprising in the *present case* the orbitals $d_{x^2-y^2}$ and d_{z^2}. The subscript g stands for 'gerade'