on relative energy scales, can only be used to predict term separations at constant Δ. They are applicable accordingly to the interpretation of spectra, since an intensity maximum approximately corresponds to a transition at fixed Δ. On the other hand, measurements involving equilibria between states give information about energies at the equilibrium geometries. These can only be predicted via estimates of total molecular energies.
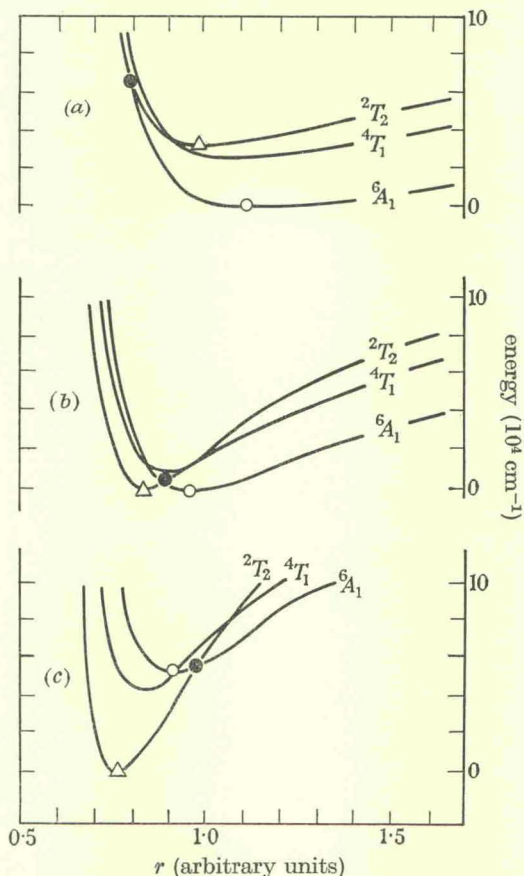

FIGURE 2. Schematic curves of total molecular energy as a function of metal–ligand distance, r. The points at which $\Delta(^6A_1)$, Δ_x and $\Delta(^2T_2)$ are evaluated as shown by $\bigcirc$, $\bullet$, $\triangle$, respectively, (a) $q = 0{\cdot}5$, $\Delta(^6A_1) < \Delta(^2T_2) < \Delta_x$; (b) $q = 1{\cdot}3$, $\Delta(^6A_1) < \Delta_x < \Delta(^2T_2)$; (c) $q = 2{\cdot}0$, $\Delta_x < \Delta(^6A_1) < \Delta(^2T_2)$.

The exact calculation of such total energies is beyond the resources of present theory. The qualitative features, however, are illustrated in figure 2, which shows three schematic potential energy curves for Mn^{2+}, calculated on the basis of a trivial generalization of a treatment given by Jørgensen (1957) of the $Mn(H_2O)_6^{2+}$ ion.* The ligands are treated as point charges of magnitude proportional to a quantity q, and the energies of the d-electrons in the octahedral component of the ligand field are superimposed on a potential of the form $k'r^{-9}-k''r^{-1}$ to yield total molecular potential

* Jørgensen's case corresponds to the choice $q = 1$ in the potential used here. Even more schematic diagrams akin to figure 2 have been given by Orgel (1960).

functions. With increase in the parameter q, the $^2T_2$ term supplants $^6A_1$ as the ground state; figure 2(b) depicts the situation in which the two states have equal energy. As in figure 1, the $^4T_1$ state is never lowest.

In each case the states $^6A_1$ and $^2T_2$ cross at some point, but in no case does this point correspond to a situation in which the minima of the two potential energy curves are coincident. Noting that Δ decreases as r increases, a necessary and quite general condition for the existence of equi-energetic ground states is seen to be

$$\Delta \,(\text{high spin}) < \Delta_x < \Delta \,(\text{low spin}).$$

The Δ values here refer to the complex in its equilibrium geometries, and Δ_x, the 'mean crossing energy', is the value of Δ at which the terms intersect. Figure 2(b) suggests that the inequalities above can be narrowed to the statement that Δ_x must lie approximately half-way between the two equilibrium values of Δ. If Δ (at given r), and the constants k' and k'' in the metal-ligand potential, have unaltered values throughout all d-electron states, then we may identify Δ_x with π, the mean pairing energy and write, more approximately,

$$\Delta \,(\text{high spin}) < \pi < \Delta \,(\text{low spin}).$$

We now consider situations resembling figure 2(b), in which the separation between the absolute zero-point energies of the $^6A_1$ and $^2T_2$ states is comparable with mean thermal energies at experimentally accessible temperatures. For convenience we shall refer to figure 2(b) as a 'crossover situation'. This appears to be in line with current usage, though we stress again that the intersection or crossover in figure 1 does not correspond to states in equilibrium.

Properties associated with almost equienergetic ground states

An obvious consequence of this situation should be a pronounced temperature dependence of the magnetic moment. For example, a simple yet realistic model upon which to base a calculation is the system of energy levels given in figure 3. Here, the ligand field is assumed to be octahedral and undistorted, but spin-orbit coupling is included since it imposes a marked temperature dependence on the magnetic moment of all low-spin d^5 complexes (Howard 1935; Kotani 1949). In the figure, ζ is the one-electron spin-orbit coupling constant, and g is one of the several parameters which should be introduced to take into account interaction with terms of higher energy. (If this complication is neglected, $g = 2$.) Although we have shown for clarity the sextet level, which is almost certainly magnetically uncomplicated, well separated from the doublet, the most interesting situations arise when their sublevels are intermingled.

The effective magnetic moment, μ, corresponding to this pattern of energy level is readily calculated. Van Vleck's equation, applied to the present situation, gives

$$\mu^2 = \frac{\frac{3}{4}g^2 + 105\,e^{-(1+E/\zeta)x} + 8x^{-1}[1 - e^{-\frac{3}{2}x}]}{1 + 2\,e^{-\frac{3}{2}x} + 3\,e^{-(1+E/\zeta)x}}, \tag{1}$$

where $x = \zeta/kT$ and E is the separation between zero-point levels of the two states.

Figure 4 plots μ against kT/ζ, as calculated from this expression, for $g = 2$ and several values of E/ζ. As foreshadowed above, marked deviations from ordinary