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Journal of Alloys and Compounds 227 (1995) 145–153

Journal of
ALLOYS
AND COMPOUNDS

Atomic spectra and instabilities of valence¹

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Received 23 January 1995; in final form 16 March 1995

Abstract

The concept of valence is discussed in relation to recent studies of the subvalence spectra of free atoms. It is argued that valence can be profoundly modified by accidental degeneracies which occur as a result of centrifugal barrier effects. Examples of “atomic hybridisation” are given, and their effects on observed spectra are discussed. Another kind of valence change occurs when a radial wavefunction is poised on the verge of orbital collapse. An example is given where a change of valence can be triggered in an atomic cluster by varying the cluster size. The origin of the effect is traced to properties of the inner short-range well in the effective atomic potential when the centrifugal term is included. It is concluded that more account needs to be taken of the underlying atomic effects and especially radial properties when setting up theories of valence for transition elements.

Keywords: Valence; Instability; Atomic spectra

1. Introduction

Although simple enough in principle, the concept of valence possesses much hidden complexity which is usually attributed to molecular forces. Since valence can only be defined once a molecule is actually formed, this attribution is logically consistent. However, the present paper will argue that there are also uncertainties of valence which originate more specifically in the properties of the constituent free atoms. Our purpose is to give some hints as to how they become apparent in the spectroscopy of free atoms.

We take “instabilities of valence” in the broadest sense to encompass both the “higher valences” which occur in chemistry generally and the phenomena grouped under such headings as intermediate valence, valence fluctuations, etc., which occur in the physics and chemistry of certain specific materials, especially those containing rare-earths. Of course, atomic physics does not contain any description of external perturbations, and cannot therefore provide a theory of intermediate valence or valence fluctuations (or even, distinguish between them). It can, however, point towards elements where instabilities in the broad sense above (i.e. including higher valence) are likely to exist.

Since an atom must contain an integral number of electrons and since an electron is of course indivisible, it is natural to think that valence should also be integral and to seek simple rules for its determination. Indeed, such rules, which rest either on the pairing of electrons with opposite spins or on the completion of shells in the Periodic Table, work very well in the majority of simple cases.

The situation becomes more complex when bond angles are discussed, and new possibilities quickly emerge. Even in a simple homologous sequence H_2X , with $X = O, S, Se, Te$ and Po , the possibility of hybridisation must be introduced in order to account for the observed departure from a simple $\pi/2$ bond angle for the first member of the sequence. Hybridisation involves superposing the s and p orbitals, and thus the electron, though indivisible, is no longer in a single “pure” state, determined by the n and l quantum numbers of atomic physics. In effect, the one-electron labels are shared.

Consequently, at least in principle, the simple rules derived from the Periodic Table to determine chemical valence become ambiguous. A calculation is now required in order to determine (on the basis of minimum energy) which of the different valences introduced by hybridisation is the more probable. For the H_2X molecules, the answer is pretty clear. The outer electronic structure of the group VI atoms

¹ Paper presented at the Chalcogenides '94 workshop, January 26th, 1994, CNRS, France.

implies a valence of 2, and this is confirmed. However, as will be explained below, group VI atoms can also exhibit higher valences [1]. We may also need to consider resonances between different kinds of bond, and then the whole subject becomes rapidly more intricate.

We note, however, that such complexities are usually regarded as a feature of molecular physics: it is assumed that the atomic situation is simple, i.e. atomic electrons are assumed to possess unique and well-defined values of n and l for free atoms. The configuration model and, by implication, the independent electron model of the free atom are understood to apply.

This understanding is based on two cornerstones of observational atomic and molecular physics, namely (i) the Periodic Table, with particular reference to the aufbau principle, and (ii) the spectroscopy of atoms in the optical range, in which only outer valence electrons are excited.

Over the past 20 years or so, a vast amount of new data on atoms have been accumulated in the vacuum-ultraviolet range of the spectrum, where inner valence electrons (the first inner subshells, which can affect chemical properties) are excited, and it has been discovered that, for very specific atoms and excitations, the independent electron model can break down dramatically. This breakdown is associated with certain features of the Periodic Table under conditions where the aufbau principle becomes misleading.

It is convenient in the present context to call the associated effects atomic hybridisation, as opposed to the molecular hybridisation discussed above.

Interestingly, the atoms involved are ones for which there are well-known problems in determining chemical valence. This arises, as one might expect, because of near-degeneracies in energy between subshells. However, what is new in contemporary atomic physics is the realisation that there exists a fairly simple model (the orbital collapse model) which allows one to understand when breakdown is likely to occur, which subshells are involved, and also explains the origin of the long periods in the Periodic Table.

The present paper argues that the root cause of many problems encountered in defining or determining valence (and especially higher valences and non-integral valence) lies in atomic physics. Certain atoms, because of their position in the Periodic Table, possess a particularly fragile n and l characterisation, and are peculiarly sensitive to their environment. They also become sensitive to the manner in which they are probed, so that unique answers cannot always be expected from different experiments.

Rather than attempt to link the recent atomic data to specific molecular valences (a truly formidable task), we pick out some good examples of the breakdown of

l characterisation in atoms, on the understanding that the reader will bear in mind the context and implications just described.

The purpose of the present paper is not to derive any new rules for valence, but rather to draw attention to some inherent complexities of the atomic model which preclude the derivation of unique and simple rules. We begin with a simple example which may assist in distinguishing between those complexities which are molecular and those which are of atomic origin.

2. Higher valence

There are many instances in chemistry where higher valences occur through hybridisation. Consider for example the group VII elements (halogens). Since their outermost configuration is p^5 (i.e. a single hole) they are expected to be monovalent. The existence of the molecules HF, F₂ and ClF confirms that this expectation is correct. Note also that, because they lie close to the rare gases, the difference in energy between the outermost s^2 and p^5 subshells is large so that little hybridisation is expected.

However, this turns out to be an oversimplification. For example, ClF₃ and BrF₃ are stable T-shaped molecules, and there exist also more complex molecules such as BrF₅ and IF₇. These polyhalogenide molecules are described in terms of bond theory in the following way: first, one constructs a sigma-bond in the usual manner, e.g. from $2p_z$ of F and $3p_z$ of Cl, where z is taken along the internuclear axis. This leaves filled orbitals such as $3p_x$ around the Cl atom. Imagine that one electron is removed from $3p_x$ to form an ion. This would leave one unpaired $3p_x$ electron, capable of forming a second Cl–F bond perpendicular to the first. Of course, the electron which was removed must also be taken up in some way, and so we attach it to another F atom, giving a structure with one ionic and two covalent bonds for ClF₃.

The example just given involves essentially molecular forces and applies even if the subshells are well-separated in energy, i.e. is not strongly dependent on the radial properties of the atoms.

Now consider the group VI elements (chalcogens). The electronic structure is s^2p^4 or $s^2p_xp_y p_z^2$ in molecular notation, so there are two unpaired electrons, implying a normal valence of 2. However, the molecules TeCl₄, TeF₆ and SF₆ also exist. The molecule SF₆, in particular, is octahedral, and requires a hybridisation of the type d^2sp^3 on the S atom in order to exist. It is interesting that some chalcogenides also exhibit mixed valence [2].

From this discussion of chalcogens, we see that higher valences of a more complex type can occur by

involving electrons from several subshells. For this to happen, the element concerned must have a structure in which several subshells are nearly degenerate in energy either for the neutral atom or for the ion. Thus, interest attaches to the spectroscopy of transition elements, and especially to cases where subshell energies may cross over as an electron is excited or removed from the system.

As will be argued below, such effects are not governed by angular properties (subshell filling) but rather by the radial equation. Specifically, the atoms which exhibit the most dramatic anomalies (orbital collapse) are those for which the effective radial potential (including the centrifugal term) possesses a double well structure.

3. The concept of quasi-particles

Taking the Hartree–Fock model as our independent electron model, we may ask what happens when we break into deeper and deeper shells by exciting them with higher and higher energy photons. The answer to this question is illustrated schematically in Fig. 1, which shows a typical photoion spectrum, one line corresponding to one ionisation threshold if the independent electron model is valid. This turns out to be completely correct in the optical range, where the energy of a photon is only great enough to excite one electron. It is also nearly true in the X-ray range, where one strong line is associated with each threshold, and only weak satellite structure is observed. This is because Heisenberg's concept of holes, i.e. quasi-particles corresponding to a vacancy in the shell structure, is applicable. It fails, however, in the intermediate energy range where inner valence electrons are excited, and where it becomes difficult to decide which line is associated with a threshold, as well as what the designation of that threshold should be. The reason for this is of course that electronic assignments

are based on the independent electron model, which attributes individual n and l values to each and every electron in the system.

4. "Optical" electrons

There is one example of optical excitation which does lead to an unexpected (though not ambiguous) result, and this example actually points us in the right direction. If we draw up the table of configurations for not only the neutral atoms, but also the singly charged ions in the d-transition elements, we find an interesting result: it is a corollary of the aufbau principle that, if one electron is removed from the atom to produce an ion, the ordering of the nl levels should remain the same in the ion as it is in the atom. Table 1, based on experimental information, shows clearly that this need not be the case. There are four elements (namely V, Co, Ni and La) from which it is impossible to remove one electron leaving the ion in its ground configuration. Quite clearly, if we accept the nl independent electron labels as meaningful, excitation of one electron cannot occur without a rearrangement of the system. In fact, it is pretty clear that the individual nl labels are not very meaningful in these cases and that the independent electron description is not satisfactory.

Consider for example the case of V: its ground configuration is $3d^34s^2$, but it takes only 0.26 eV to promote it to $3d^44s$, a state of different valence. Indeed, closer examination tells us that these two configurations cannot really be separated from each other because they have the same parity and are prone to mixing. Such mixing effects do not necessarily alter the normal valence of the atom, but they may facilitate higher valences, as discussed before.

Situations similar to the one just described can also be created by subvalence excitation: with an inner shell excited, barium resembles lanthanum as far as its

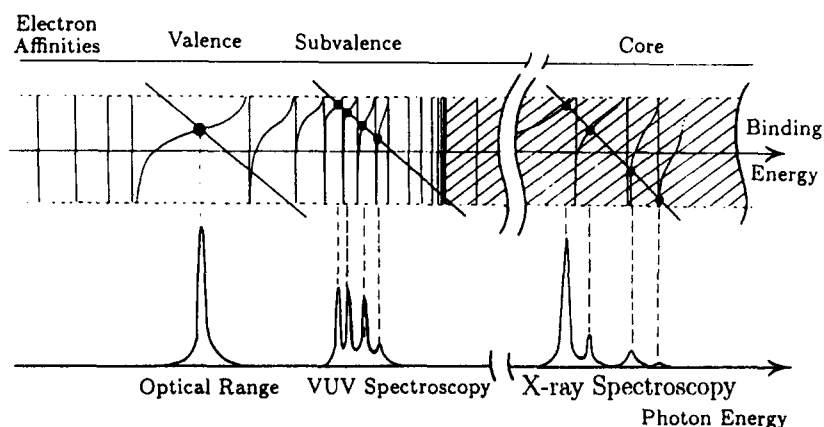


Fig. 1. The behaviour of a typical photoion spectrum for optical, subvalence and deep X-ray excitation: graphical solutions of the many-body Dyson equation are indicated schematically.

Table 1

Ground configurations of the atoms and ions belonging to the first long periods (transition elements)

Ca	...4s ²	...4s	Sr	...5s ²	...5s	Ba	...6s ²	...6s
Sc	3d4 ²	3d4s	Y	4d5s ²	...5s ²	La	5d6s ²	...5d ²
Ti	3d ² 4s ²	3d ² 4s	Zr	4d ² 5s ²	4d ² 5s	Hf	5d ² 6s ²	5d6s ²
V	3d ³ 4s ²	3d ³ ...	Nb	4d ³ 5s	4d ³ ...	Ta	5d ³ 6s ²	5d ³ 6s
Cr	3d ³ 4s	3d ⁵ ...	Mo	4d ⁴ 5s	4d ⁵ ...	W	5d ⁴ 6s ²	5d ⁴ 6s
Mn	3d ⁵ 4s ²	3d ⁵ 4s	Tc	4d ⁵ 5s ²	4d ⁵ 5s	Re	5d ⁵ 5s ²	5d ⁵ 6s
Fe	3d ⁶ 4s ²	3d ⁶ 4s	Ru	4d ⁷ 5s	4d ⁷ ...	Os	5d ⁶ 6s ²	5d ⁶ 6s
Co	3d ⁷ 4s ²	3d ⁸ ...	Rh	4d ⁸ 5s	4d ⁸ ...	Ir	5d ⁷ 6s ²	–
Ni	3d ⁸ 4s ²	3d ⁹ ...	Pd	4d ¹⁰ ...	4d ⁹ ...	Pt	5d ⁹ 6s	5d ⁹
Cu	3d ¹⁰ 4s	3d ¹⁰ ...	Ag	4d ¹⁰ 5s	4d ¹⁰	Au	5d ¹⁰ 6s	5d ¹⁰
Zn	3d ¹⁰ 4s ²	3d ¹⁰ 4s	Cd	4d ¹⁰ 5s ²	4d ¹⁰ 5s	Hg	5d ¹⁰ 6s ²	5d ¹⁰ 6s

outer electrons are concerned. Consequently, they seek to arrange themselves in a configuration involving 5d electrons, such as 5d6s or 5d² rather than remaining 6s² as in the ground state. In other words, a simple, one-electron excitation scheme becomes impossible to achieve.

The situation for filling of the f subshell is in principle simpler than in Table 1 since there is no analogue of s–d competition, and there are no states of the same parity at the same energy with which the f states could mix. However, a careful study reveals another kind of complexity [3]: the f orbitals are eigenstates of a double well radial potential, which is why their filling occurs deep inside the atom. Consequently, the f-orbitals are bimodal, with an amplitude deep inside the atom and an amplitude at its surface. This means that hybridisation with orbitals from neighbouring atoms or with the conduction band (as may occur in compounds and solids) can involve a fraction of the electronic charge which is external, while another part of the atomic orbital retains its quasi-atomic properties (i.e. is localised).

The situation in Fig. 1 can thus be summarised as follows.

(a) The incident photon may only possess enough energy to excite one electron. This is optical spectroscopy, and is unlikely to yield much information on many-body excitation, since the energy is insufficient to drive cooperative modes. Only one line is observed, corresponding to the excitation of one particle; dramatic rearrangements of the shell structure (see Table 1) are possible, but rare.

(b) The incident photon may possess enough energy to excite the deepest shells. This is X-ray spectroscopy and is, again, unlikely to provide much information on breakdown of the *nl* quantum numbers. The reason here is that the initial state wavefunction is much smaller than that of the final state, so that the electron escapes very fast, leaving behind a well-characterised vacancy from which it is screened by all the interven-

ing shells. This vacancy behaves as a quasi-particle. Experimentally, one sees a single line, surrounded by a few satellites, which are a measure of the small breakdown of the quasi-particle approximation.

(c) The incident electron may possess sufficient energy to excite a subvalence electron but not enough to excite a deep shell. In this range, the spatial overlap between the vacancy and the excited state wavefunction is greatest. Rearrangements can occur while the electron is escaping, and instead of a single line one can find a jumble of features into which the quasi-particle line has fragmented. We say that the quasi-particle model itself has broken down.

The description above is backed up by experiments and calculations, which both point to the fact that the vacuum ultraviolet and soft X-ray ranges of the electromagnetic spectrum are ideally matched to the study of quasi-particle breakdown. This energy range is also of interest for the chemistry of many elements since it involves the excitation of the inner valence electrons.

In core-level spectroscopy, one is determining the configuration of the outer electrons in the presence of the core hole. For free atoms, this is readily connected to ground-state properties, since *ab initio* calculations can be performed for both the initial and the final state. Indeed, as pointed out above, both may be relevant in a discussion of higher valence. When determining valences in the solid, however, a procedure is needed to recover the initial-state situation from observations which involve a core-excited final configuration. This is achieved via a semi-empirical procedure devised by Gunnarsson and Schönhammer [4] which, however, involves the use of adjustable parameters to represent, for example, hybridisation with the conduction band. Since the latter is a parametric method, it is not predictive and does not tell us in advance which atoms are liable to possess instabilities of valence. This kind of information is implicit in atomic physics (see Table 2).

Table 2
The quasi-periodic table of Smith and Kmetko

Magnetism															
4f	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5f	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3d	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				
4d	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd				
5d	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg				

Conductivity

5. Spectroscopic implications for atoms

The conservation of angular momentum (i.e. the validity of the l quantum number) is a property of central fields. However, the central field is only an approximation for real many-electron atoms. If it applies, then we can define l unambiguously for each electron, and electrons can be regarded as dynamically independent. Within this atomic framework, the subsequent step of defining valence becomes a simpler problem.

Unfortunately, atomic electrons can never be regarded as dynamically independent even for an isolated many-electron atom. The degree of approximation involved varies widely according to the atom concerned. The study of atomic spectra gives some idea of the validity of approximations which underpin the definition of valence.

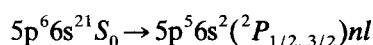
For each electron in a many-electron system, there are in fact two ways to define n . One is to apply an approximate Rydberg formula $E_\infty - E_n = R/[(n - \mu)^2]$ in which the quantum defect μ has been introduced and to use the energy of the state E_n to extract n . The other is to count the nodes of the wavefunctions. Usually, these two methods are consistent, provided the approximate constant μ is used to absorb the influence of the core. There are, however, situations in which μ ceases to be a weakly varying quantity. Discrepancies arise between the methods of defining n which can be traced to centrifugal barrier effects in the free atom.

Let us now consider some examples of how this behaviour manifests itself in spectra. In molecular physics, the emergence of clean Rydberg series, devoid of rovibronic structure, is interpreted as a sign of atomicity. In atomic physics, however, we do not always find clean Rydberg series. When we do not, this is often a sign that the independent electron model has

broken down (non-Rydberg spectroscopy [3]). Heavy perturbations or modifications of the Rydberg spectrum, the disappearance of series or the emergence of unexpected, additional series are all indications that the nl characterisation of electrons is breaking down, i.e. that configurations are mixed in the free atom.

Effects involving n will be dealt with in Section 7 below. We give here an example of the complete breakdown of l characterisation, which also arises from centrifugal effects, and is illustrated in Fig. 2.

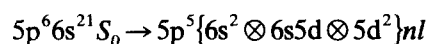
This figure shows the 5p excitation spectrum of BaI. If the independent electron model were applicable, then the excitation scheme would be



which gives rise to series converging on just two limits namely ${}^2P_{1/2}$ and ${}^2P_{3/2}$ of the parent ion. In fact, a multitude of series limits is observed (see Fig. 2), and therefore the model is clearly inadequate.

An explanation can be sought in terms of Table 1 above: it was pointed out that one cannot remove an electron from La (whose ground state involves only one 5d electron) without producing an ion whose ground configuration contains two 5d electrons. In other words, the 5d orbital becomes rapidly more binding than 6s as the charge at the centre increases (the real reason for this will be explained in Section 7 below). When an electron from the inner shell of BaI is excited, it begins to resemble LaI because of the extra charge. Consequently, the 6s and 5d orbitals come very close in energy, and strong mixing sets in. Another way of looking at this is that the 6s and 5d electrons cease to be dynamically independent in BaI: when a 5p electron is excited, the $6s^2$ subshell is shattered, and the multitude of Rydberg series observed converge to parent ion states which are, in a sense, its fragments.

Formally, we represent the excitations as:



where a multitude of parent ion limits can now arise, because it is no longer possible to distinguish between 6s and 5d electrons of the core in the presence of a 5p vacancy. Despite this complete breakdown of the $6s^2$ subshell structure, some rules persist: the total angular momentum of the core is found to remain a good quantum number and, indeed, it is through mixing with the ${}^2P_{1/2, 3/2}$ states of the undisturbed core that the complex excitation scheme arises. Thus, it has been found [5] that the degree of 2P character of the mixed states is a good guide to whether conspicuous series are observed.

The dramatic effect of $6s \otimes 5d$ mixing appears most



Fig. 2. The 5p excitation spectrum of barium, showing the extremely complex, overlapping manifold of Rydberg series which arises from shattering of the 6s subshell.

clearly in the photoabsorption spectrum of Fig. 2: instead of just two series limits expected on the independent electron model, as many as fifteen series limits have been picked out in this spectrum [6].

There are other interesting effects such as an enhancement of double ionisation due to this mixing [7].

6. Supernumerary Rydberg series

In the example just given, supernumerary series are excited because of a near-degeneracy of parent ion states belonging to two or more different configurations. Another situation which can occur is that an inner valence spectrum becomes degenerate in energy with a manifold of doubly-excited states. This situation is most readily studied by plotting the inner shell and double-ionisation thresholds as a function of atomic number, which reveals crossing points for certain specific atoms. One can then conduct a series of investigations for each element near the crossings. Examples of such graphs are shown in Fig. 3.

By a detailed study of the spectra of atoms near the crossings [8], we have shown that several possibilities exist, which demonstrate how breakdown of the independent electron model sets in as the crossings are approached.

(i) For atoms whose inner-shell spectrum is well below the double-ionisation limit, long Rydberg series are found, converging on the inner-shell threshold.

(ii) As the inner-shell limits approach the double-ionisation limits from below, the series become more complex and veer off their normal course to converge on the nearest accessible series limits for double excitation. Since these become more and more numerous as the double-ionisation threshold is approached, the spectrum becomes extremely rich. A good example of this behaviour is found in the 5d spectrum of Tl [9].

(iii) As the inner shell spectrum rises above the double-ionisation limit, strong Auger broadening of the inner-shell spectrum is observed, and most of the structure is wiped out. Indeed, many expected subvalence shell series disappear from view. Instead, one sees quasi-continuous absorption with only diffuse features, and there is a dramatic enhancement of photo-double ionisation in which two valence electrons are ejected.

The examples in Fig. 3 are drawn from the 3d and 4d transition periods. Note that the subvalence excitation thresholds (which correspond to $l = 2$ vacancies) travel fast in energy as a function of atomic number, whereas the double and triple ionisation thresholds are fairly constant in energy over the range concerned. Nearly exact crossings occur for Ga and In, so one might expect the next crossing to occur for Tl. In fact, it lies between Tl and Pb, the filling of the 4f subshell having occurred in between. Thus Hg, Tl and Pb are elements whose chemistry is likely to be affected by the properties of the 5d subshell.

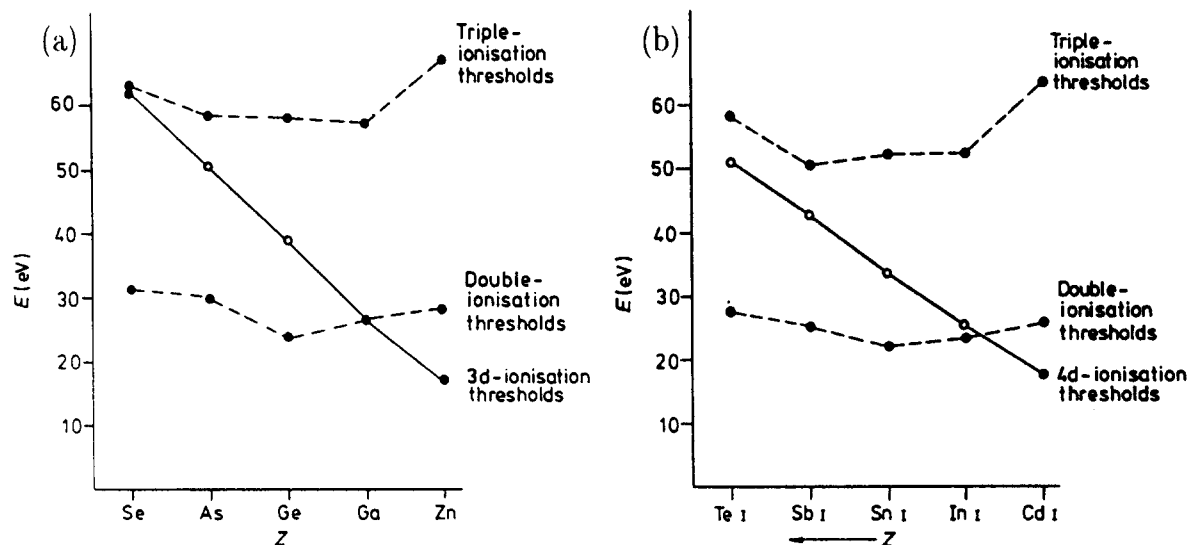


Fig. 3. Plot of the ionisation thresholds for inner shell, double and triple photoionisation, showing the degeneracies which occur for elements of (a) the 3d and (b) the 4d sequences.

7. Centrifugal barrier effects

Much of the behaviour described in the previous sections is due to the fact that electrons in different angular momentum states respond differently to changes in the effective charge of the system. These differences in polarisability are due to differences in the magnitude of the centrifugal barrier in the effective radial potential:

$$V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$$

experienced by each electron. The repulsive centrifugal term grows fast with l , and is now known to be responsible for deep shell filling and the formation of the long periods in the Periodic Table (see, for example, Ref. [10]).

The reason for this can be traced to the form of $V_{\text{eff}}(r)$ for complex atoms and $l=2$ or $l=3$ electrons. Since there are many different effects which result from the balance between electrostatic attraction and centrifugal repulsion, and since these effects also depend markedly on the value of l , there is not enough space in the present brief survey to discuss all the situations which arise. We therefore confine our discussion to some general remarks and to one specific example, which occurs for $l=3$.

From studies of magnetism and conductivity in solids, a "quasi-Periodic Table" has been devised [11] which describes many related properties of the elements (see Table 2). In particular, there is a broad curve which sweeps across this table and separates the elements which are good conductors from those which

are good magnets. This curve effectively is the locus of the first-order Mott transition between localised and itinerant behaviour, and this is related to the fact that, in atoms with $l=3$, the effective potential develops a deep and narrow, short-range inner well which can either trap f electrons deep inside the atom or can be empty of bound states for just a small change in the environment. Indeed, it is even possible for a $4f$ electron to tunnel between this inner localised state and a delocalised or extended state in the outer reaches of the atom. One cannot, in this situation, use a Rydberg formula to determine the principal quantum number n , and this is indeed not surprising since the inner well is definitely non-coulombic.

When it is inside the atom, the electron is in a quasi-atomic orbital, and remains localised on a specific atomic site. When it is in the outer reaches, it can hybridise with other electrons and join, say, the conduction band, if the atom is inside a solid. If the electron is in a critical state, with a wavefunction which (for the equivalent free atom) possesses significant amplitudes both in the inner well and in the outer reaches of the atom, then in the condensed phase we may find a non-integral charge localised on the atomic site, with the rest entering the conduction band. Whether or not this happens depends very critically on the depth of the inner well times its width squared. This product fixes the binding strength in a short-range well, i.e. it determines the number of bound states of the inner well [3].

One is not used to thinking of atomic potential wells containing only a finite number of bound states. The important point is that the deep inner well is a short-range well, and it is even possible for an asymmetric

short-range well to be nearly empty of states, with just one bound state very close to the mouth of the well. If the well is made slightly shallower, the orbital is expelled into the outer reaches, but if it is made slightly deeper, the orbital collapses deep inside the atom. Atoms on the edge of fulfilling the quantum-mechanical condition for orbital collapse are those which may possess non-integral valence, and pronounced instabilities of valence.

When the quasi-Periodic Table is examined, atoms along the ridge tend to lie close to this situation, as is evidenced by the fact that some of them are unstable under pressure. For example, Ce experiences an $\alpha \rightarrow \gamma$ isomorphic phase transition at a pressure of nearly one kilobar. It has been shown by ab initio calculations that, if an atomic model is used to describe valence instabilities, the order of magnitude of the pressure required to trigger the phase transition is in agreement with the experimental value [12].

8. Spectroscopy of clusters

Another approach is to control the environment of the atom by preparing clusters of different sizes, and it

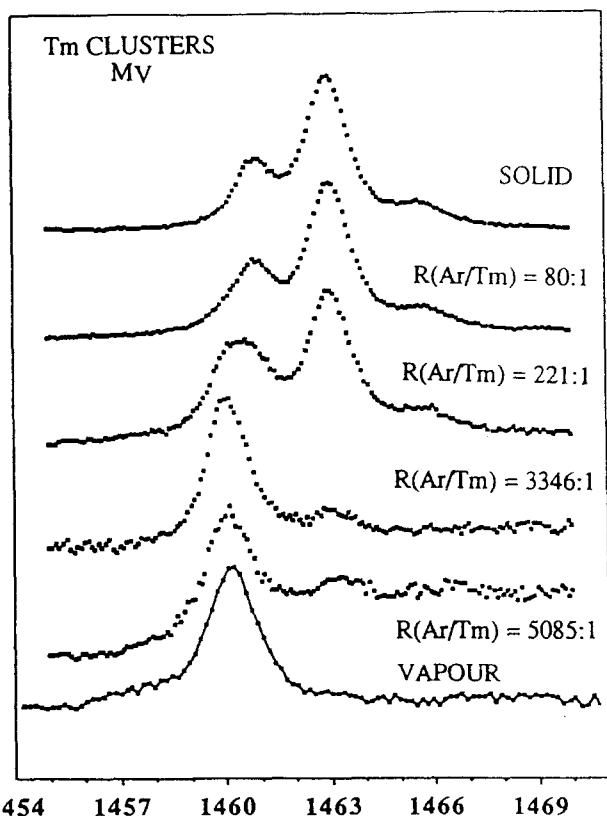


Fig. 4. Spectra of 3d excitation in thulium in different phases. The spectrum of the atom and of the solid are shown, with in between them spectra corresponding to different cluster sizes, displaced on a horizontal scale so that they tend from the atomic to the condensed matter limit.

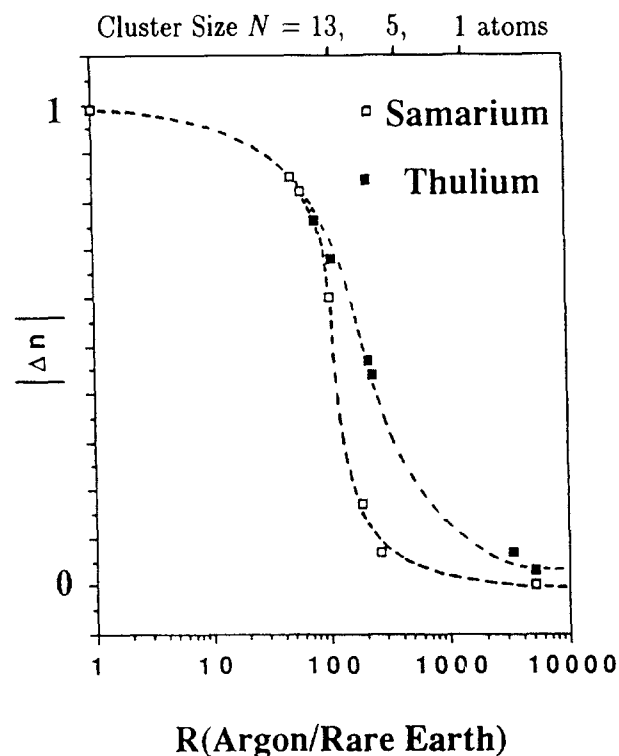
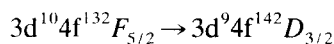


Fig. 5. The valence for clusters of Tm and Sm as determined by X-ray spectroscopy, plotted as a function of the number of atoms in the first coordination cell.

has been found that, for appropriately chosen atoms, a valence change can actually be triggered in this way. An example is shown in Fig. 4, which demonstrates how clusters of thulium atoms behave as a function of size, when probed by inner shell spectroscopy from the 3d subshell.

This is a particularly nice example, because thulium atoms contain 13 4f electrons, which means that only one transition from the 3d subshell occurs, namely:



as long as there are 13 electrons in the 4f subshell. If, however, the number of 4f electrons drops to 12 as a result of a change of valence, then additional lines are seen. The spectrum near the allowed line is shown in Fig. 4, and we can conclude merely by inspection of the spectra that a valence change occurs. It actually appears for a small cluster size (between 5 and 13 atoms), well before the solid state limit is reached, as is more clearly seen in Fig. 5, which shows the valence change as determined by X-ray spectroscopy as a function of the cluster size for both Sm and Tm atoms [13].

9. Conclusion

We have given a number of examples where uncertainties of valence or intermediate valence effects

may occur as a result of properties of many-electron atoms. In general, these effects are related to orbital-collapse phenomena [14], and are therefore confined to the long periods of the periodic table.

It is likely that atomic effects of this kind are already lurking in the background of theories of molecular valence and remain to be interpreted. Thus, in a discussion of H_2X molecules, where X is a Group VI atom, Coulson [1] in his monograph on the shape and structure of molecules remarks: “there are two reasons why the valence angle in H_2O exceeds 90° . One is the use of hybrids of s and p, and the other is purely electrostatic ... since the electronegativity difference decreases as we go down the group, we expect the electrostatic part of the increase in valence angle to decrease as well. But there is as yet no satisfactory simple explanation of the fact that, except for H_2O , all the valence angles are close to 90° , implying p bonds with little or no hybridisation.” For other molecules involving X atoms, he goes on to consider s–d hybridisation and comments: “... part of the difficulty lies in the fact that, for an isolated S atom, the 3d orbitals lie well outside the 3s and 3p orbitals, so that, unless some mechanism exists for compressing the d orbitals, and not the s and p orbitals, effective hybridisation cannot be achieved. One such mechanism is known: if the S atom is partly ionised ... it appears that the d orbitals contract. The matter is still not settled ...”.

We have quoted this passage at some length because selective d-orbital collapse resulting from centrifugal barrier effects is now a well-known atomic effect, and has also been studied in homologous atomic sequences [15]. An interplay between atomic centrifugal barrier effects and molecular fields is to be expected.

Such effects are distinct from the existence of higher valences as a result of molecular hybridisation. They

point to the need to combine an understanding of orbital collapse in short-range atomic potentials with appropriate models for molecular and condensed phases, so as to take on board current understanding of the atomic phenomena which control the polarisability of subshells with high angular momentum.

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