

a0=0.529177A

n = 1 2 3 4 5 6  
n\* = 1 2 3 3.7 4.0 4.2

1s 2  
2s 2  
2p 6  
3s 2  
3p 6  
3d 10  
4s 2  
4p 6  
4d 10  
5s 2  
5p 1

In3+イオンの5sを考える。

n<4 28\*1.0

1s 2  
2s 2  
2p 6  
3s 2  
3p 6  
3d 10

n=4 18\*0.85

4s 2  
4p 6  
4d 10  
5s 0

Z=49

s = 18\*0.85 + 28\*1.0 = 43.3

Z\* = 5.7

rmax = a0/Z\* \* n\*^2 = 0.093 \* 4^2A = 1.488A

In原子の5sを考える。

n<4 28\*1.0

1s 2  
2s 2  
2p 6  
3s 2  
3p 6  
3d 10

n=4 18\*0.85

4s 2

4p 6

4d 10

n=5 2\*0.35

5s 3

Z=49

s = 18\*0.85 + 28\*1.0 + 2\*0.35 = 44

Z\* = 5

a\* = a0/Z\* \* n^2 = 0.11 \* 4.7\*4.7A = 0.517 A = 1.693

$$R = N r e^{\frac{n^* - 1 - (z-s)r}{n^* a_0}} \quad a = \frac{\cancel{a}^{n^*}}{z-s} a_0$$

$$r^2 R^2 \text{ and } r^{2n^*} e^{\frac{-2r}{a}}$$

$$\frac{\partial}{\partial r} (r^2 R^2) = \left(2n^* - \frac{2}{a}r\right) r = 0$$

$$r_{\max} = n^* a_0 \quad \frac{n^{*2}}{z-s} a_0 \quad 0.53A$$

~~$$\frac{\partial}{\partial r} R^2 = \left(2n^* - 2 - \frac{2}{a}r\right) = 0$$~~

$$r = a(n^* - 1)$$

Wiley International Edition

# QUANTUM

# CHEMISTRY

BY

**HENRY EYRING**

DEAN OF GRADUATE SCHOOL  
*University of Utah*

◆

**THE LATE JOHN WALTER**

PALMER PHYSICAL LABORATORY  
*Princeton University*

◆

**GEORGE E. KIMBALL**

PROFESSOR OF CHEMISTRY  
*Columbia University*

◆

**JOHN WILEY & SONS, INC.**  
NEW YORK

LONDON

TOPPAN COMPANY, LTD., TOKYO, JAPAN

In the presence of a magnetic field, the energy depends also on  $M$ . The observed phenomena in the Zeeman effect are explained by the selection rule for  $M$

$$\Delta M = 0, \pm 1 \quad 9.91$$

this selection rule being derivable in the same manner as the selection rule for  $m$  in the theory of the hydrogen atom. The selection rule  $\Delta M = 0$  corresponds to the non-vanishing of the  $z$  component of the dipole moment integral; the light emitted during a transition for which  $\Delta M = 0$  is polarized along the  $z$  axis (the direction of the magnetic field). Similarly, for transitions for which  $\Delta M = \pm 1$ , the emitted light is circularly polarized in the  $xy$  plane. In passing, we might mention that investigations of the Zeeman effect provide one of the most powerful tools for the determination of the characteristics of the states involved in atomic spectra.

9k. The Radial Portion of the Atomic Orbitals. Up to the present we have not specified the exact nature of our atomic orbitals, aside from the specification that the angular portion of the orbitals would be the ordinary spherical harmonics, since they were assumed to arise from the solution of a central field problem. For any quantitative calculation of energy levels some form must be chosen for the radial portion of the orbital. The best one-electron orbitals are found by the method of Hartree, which is discussed in the next section. In approximate work it is often desirable to use orbitals which, although less accurate than those obtained by Hartree's method, are simpler in form and hence easier to use. For example, Zener<sup>10</sup> and Slater<sup>11</sup> have used orbitals of the form

$$Nr^{(n^*-1)}e^{-(Z-s)\frac{r}{n^*a_0}}Y(l, m|\theta, \varphi) \quad 9.92$$

where  $n^*$  and  $s$  are adjustable constants and  $N$  is a normalizing factor. These eigenfunctions are solutions of the central field problem where  $V(r)$  is given by the relation

$$V(r) = -\frac{(Z-s)e^2}{r} + \frac{n^*(n^*-1)h^2}{8\pi^2 mr^2} \quad 9.93$$

For large values of  $r$  this approaches

$$V(r) \sim -\frac{(Z-s)e^2}{r} \quad 9.94$$

corresponding to a screening of the nucleus equivalent to  $s$  atomic units;

<sup>10</sup> C. Zener, *Phys. Rev.*, **36**, 51 (1930).

<sup>11</sup> J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

in other words, the effective nuclear charge is equal to  $Z - s$ . From its resemblance to the quantum number  $n$  of the hydrogen atom,  $n^*$  is known as the "effective quantum number." Qualitatively, the eigenfunctions 9.92 differ from the hydrogen eigenfunctions in that there are no nodes in the radial portion, whereas the hydrogen eigenfunctions have  $n - l - 1$  nodes.

By varying  $n^*$  and  $s$  so as to minimize the energy, Slater has been able to give the following rules for the determination of these constants:

1.  $n^*$  is assigned according to the following table, according to the value of the real quantum number  $n$ :

$n =$	1	2	3	4	5	6
$n^* =$	1	2	3	3.7	4.0	4.2

2. For determining  $s$ , the electrons are divided into the following groups:  $1s$ ;  $2s, 2p$ ;  $3s, 3p$ ;  $3d$ ;  $4s, 4p$ ;  $4d, 4f$ ;  $\dots$

3. The shielding constant  $s$  is formed, for any group of electrons, from the following contributions:

- Nothing from any shell outside the one considered.
- An amount 0.35 from each other electron in the group considered (except in the  $1s$  group, where 0.30 is used).
- If the shell considered is an  $s$  or  $p$  shell, an amount 0.85 from each electron with principal quantum number less by 1, and an amount 1.00 from each electron still farther in; but if the shell is a  $d$  or  $f$  shell, an amount 1.00 from each electron inside it.

For example, carbon has two  $1s$  electrons, two  $2s$  electrons, and two  $2p$  electrons. The approximate radial orbital (unnormalized) for a  $1s$  electron is, according to the above rules:

$$\varphi(1s) \sim e^{-5.70 \frac{r}{a_0}}$$

while for a  $2s$  or  $2p$  electron the radial function is

$$\varphi(2s) = \varphi(2p) \sim re^{-\frac{3.25r}{2a_0}}$$

Since the constants in these functions were determined by the use of experimental data, the functions will be satisfactory for rough quantitative calculations. Various other sets of screening constants have been proposed for use in wave functions of the above type, for example, those of Pauling and Sherman.<sup>12</sup>

91. The Hartree Method. According to our discussion of the helium atom in Chapter VII, the best wave functions for an atomic system

<sup>12</sup> L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

**Carrier generation in wide-gap oxides  
with amorphous or nanometer-sized structure**

**by**

**Naoto KIKUCHI**

those obtained by Hartree's method, are simpler in form and hence easier to use in approximate work. Slater have used orbitals of the form

$$R_{nl}(r) = N r^{(n^* - 1)} e^{-(Z-s)\frac{r}{n^* a_0}} \quad (1)$$

where  $n^*$  and  $s$  are adjustable constants and  $N$  is a normalizing factor. Figure 6-7 summarized s-orbital radii of p-block cations calculated using eq. (1)

#### 6.4. Magnitude of the overlap of s-orbitals

Figure 6-8 shows the relationship between distance (  $d$  ) of the neighboring cation of the crystalline oxides and s-orbital radii (  $R$  ) of the s-orbital of p-block cations, where  $R = r_A + r_B$  and  $r_A, r_B$  are s-orbital radii of p-block cations (  $M_A, M_B$  ). Dotted line in the figure indicates  $R=d$ . This figure shows that large overlap between the s-orbitals of the neighboring cations is attained in oxides reported as amorphous conductors except  $In_2O_3$ . On the other hand the magnitude of the overlap between the orbitals of three oxides examined in chapter 3 is smaller than that of the oxides previously reported. Since radii of the s-orbital in  $Ag^+$  ion or  $Cd^{2+}$  ion are relatively large in comparison with those of  $Sn^{4+}$  or  $Sb^{5+}$ , it is possible to overlap of s-orbitals largely. There is no information about a reason why the magnitude of the overlap in  $In_2O_3$  is small. However distance between the neighboring In atoms may be short, since concentration of oxygen in a- $In_2O_3$  is small in comparison with the stoichiometric composition.

The crystal structure of  $Zn_2SnO_4$  is inverse spinel  $[Zn(Zn,Sn)O_4]$  which contained rutile chains along [110] direction and chains of edge sharing octahedra in which  $Zn^{2+}$  and  $Sn^{4+}$  ions are centered. (Figure 6-5) Because the occupancy in the cation sites of the rutile chains is  $\sim 0.5$  for both cations. Distance between  $Zn^{2+}$  and  $Sn^{4+}$  in rutile chain is 305.8 pm.

•  $ZnSb_2O_6$  ( $P4_2/mnm$ )<sup>8)</sup>

The crystal structure of  $ZnSb_2O_6$  is trirutile which contains rutile chains running along c-axis. In  $ZnSb_2O_6$  system, rutile chains consist of  $Zn^{2+}$  and  $Sb^{5+}$ . Figure 6-6 shows the crystal structure of  $ZnSb_2O_6$  trirutile. Distance between  $Zn^{2+}$  and  $Sb^{5+}$  in the rutile chain is 307.7 pm, and that between  $Sb^{5+}$  and  $Sb^{5+}$  is 308.6 pm.

•  $InSbO_4$ <sup>9,10)</sup>

The crystal of  $InSbO_4$  is not random rutile structure precisely. Crystal structure of  $InSbO_4$  had been reported by Bayed as rutile-type with lattice constants of  $a=474$  pm and  $c=321.5$  pm. Then, it was found the crystal system of  $InSbO_4$  to be monoclinic by Varfolomeev et al.. Therefore it is supposed that the structure of  $InSbO_4$  is distorted, random-rutile structure. In this study, it is assumed the crystal structure of  $InSbO_4$  to be rutile-type for the simplified discussions and the distance between neighboring cations had been calculated.

Rutile structure contains rutile chains which consist of  $In^{3+}$  and  $Sb^{5+}$  running along c-axis, where the occupancy of the cation sites in rutile structure is  $\sim 0.5$  for both cations because of random-rutile structure. Distance between both cations is 322 pm.

### 6.3. Orbital radii estimated from Slater type orbitals<sup>11)</sup>

The best one-electron orbitals are found by the method of Hartree. However it is often desirable to use orbitals which, although less accurate than

## References

- 1) N.Kikuchi, H.Hosono, H.Kawazoe, K.Oyoshi and S.Hishita, *J. Am. Ceram. Soc.*, **80**, 22-26 (1997)
- 2) W.D.Kingery, H.K.Bowen and D.R.Uhlmann, "Introduction to Ceramics 2nd ed." John Wiley&Sons (1975) pp.91-94
- 3) Y.Sawada, *Display '96-9*, 33-39 (1996) (in Japanese)
- 4) M.Yasukawa, H.Hosono, N.Ueda and H.Kawazoe, *J. Ceram. Soc. Jpn.* **103**, 455-59(1995)
- 5) M.Trömel, *Z. Anorg. Allg. Chem.* **371**, 237-247 (1969)
- 6) P.Tarte, *J. Inorg. Nucl. Chem.* **27**, 1933-1938 (1965)
- 7) T.F.W.Barth and E.Posnjak, *Z. Kristallogr. Kristallgeo. Kristallphys. Kristallchem.* **82**, 325-341 (1932)
- 8) A.Bystrooem, B.Hoek and B.Mason, *Arkiv Kemi, Min. Geol.* **15B**, 1-8 (1942)
- 9) G.Bayer, *Z. Kristallogr.* **118**, 158-160 (1963)
- 10) M.B.Varfolomeev, M.N.Sotnikova, V.E.Plyushchev, and B.V.Strizhkov, *Inorg. Mater.* **11**, 1209 (1975)
- 11) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley&Sons (1944) pp. 162-163

n	I B	II B	III A	IV A	V A
4	<b>Cu</b> 195.7	<b>Zn</b> 166.5 (2+) 154.1	<b>Ga</b> 144.8 (3+) 127.1	<b>Ge</b> 128.2 (4+) 108.1	<b>As</b> 115.0 (3+) 103.5 (5+) 94.1
5	<b>Ag</b> 240.2	<b>Cd</b> 194.6 (2+) 180.1	<b>In</b> 169.3 (3+) 148.5	<b>Sn</b> 149.8 (2+) 141.1 (4+) 126.3	<b>Sb</b> 134.4 (3+) 120.9 (5+) 109.9
6	<b>Au</b> 252.2	<b>Hg</b> 214.5 (2+) 198.5	<b>Tl</b> 186.6 (3+) 163.7	<b>Pb</b> 165.2 (2+) 155.5 (4+) 139.3	<b>Bi</b> 148.1 (3+) 133.3 (5+) 121.2

Fig. 6-7 STO radius of ns orbitals. The top indicates the radius of atom and the other indicate those of ions. ( unit: pm )