Theoretical Determination of the Electronic Polarizability of Lithium and Scandium

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Different experimental investigations, *e.g.* of the crystal structure of certain Al-Si-Me compounds [1], make it plausible to assume that the electronic polarizability of atoms and ions with partly filled *d*-shells (transition elements) should be considerably larger than the polarizability of closed shell atoms. This assumption can be supported by simple, theoretical considerations. However, no detailed theoretical investigation of this problem seems to have been published before. As the problem is of great interest in several connections, we have made an attempt to find the order of magnitude of this polarizability from a simple perturbation calculation.

The electronic polarizability of atoms with rare-gas-like configurations, *i.e.* s^2p^6 and $s^2p^6d^{10}$, has recently been treated as a perturbation problem by Sternheimer [2]. We have carried out a similar perturbation calculation for the case of atoms with one electron outside the closed shells and applied the result to Li $1s^22s$ and Sc $3d\,4s^2$. Using an one-electron model the unperturbed wave function can be written as a single Slater determinant of unperturbed one-electron functions φ_i. The first-order perturbation of these functions, φ_i', is determined by the equation

$$(H_0 - E_0)\ \varphi_i' = -V\ \varphi_i, \qquad (1)$$

where V is the perturbing potential. The electronic polarizability α is

$$\alpha = -\frac{2}{E^2}\sum_i \int \varphi_i^*\, V\, \varphi_i'\, d\tau \qquad (2)$$

where the sum is to be taken over all filled orbitals.

In the case of Sc the $3d$ orbital of the unperturbed atom cannot be given a definite m-value. We have shown, however, that the correct zeroth-order wave function for the $3d$ electron corresponds to $m = 0$. The differential equations (1) have been solved by numerical methods, using the Swedish electronic digital computor BESK. Hitherto, we have programmed the problem for one-electron orbitals of the simple analytic form $r^n e^{-\mu r}$. However, the programme can easily be modified so that also numerically given orbitals can be used. As the computed value of α is strongly depending on the choice of unperturbed functions, we can only expect to get a rough estimate by the use of simple analytical orbitals. As a check on our programme we have computed the polarizability of Ca^{2+}, previously calculated by Sternheimer [2].

Preliminary results for the polarizabilities of Li and Sc are given in Table 1. In the case of Li the contribution to α from the inner shell is negligible. In the case

Table 1. Calculated and experimental values of the electronic polarizability α.

Atom	α in units 10^{-24} cm^3	Method	Author
Li	16 ± 3	exptl.	Drechsler and Müller [4]
	20	theor., μ chosen to fit the best SCF orb.	present inv.
Ca^{2+}	0.47—1.1	exptl.	Tessmann, see [2]
	0.73	theor., SCF orb.	Sternheimer [2]
	0.83	theor., μ chosen to fit the best SCF orb.	present inv.
Ca	92	theor., μ from Slater's rules	present inv.
	52	theor., μ chosen to fit SCF orb.	present inv.
Sc	90	theor., μ from Slater's rules	present inv.

of Sc the same is true and the main contribution orginates from $3d\ 4s^2$. In order to discriminate between $3d$ and $4s^2$ we have also computed a of Ca $4s^2$. Table 1 shows that a of Ca and Sc both are much larger than a of Ca^{2+}.

An extension of the present investigation to include atoms with several d-electrons outside the closed shell is going on. It would be of special interest to look at Ni, for which an experimental value of a is available [3].

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1. Spiegelberg, P. *Private communication.*
2. Sternheimer, R. M. *Phys. Rev.* **96** (1954) 951.
3. Liepack, H. and Drechsler, M. *Naturwiss.* **43** (1956) 52.
4. Drechsler, M. and Müller, E. W. *Z. Physik* **132** (1952) 195.

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Note on the Crystal Structures of Hexagonal HgO and Hg_2O_2NaI

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The hexagonal modification of mercury (II)oxide and the compound Hg_2O_2NaI have been prepared according to Laruelle [1] and studied by X-ray diffraction methods.

HgO. Hexagonal form. Space group $P3_121$ No. 152. Unit cell dimensions $a = 3.577$ Å, $c = 8.681$ Å in agreement with the values given by Laruelle. The cell content is 3 formula units of HgO. The positions of the mercury atoms have been derived by means of trial methods from powder data registered with a Geiger-Mueller diffractometer using Cu$K\alpha$ radiation. A probable arrangement of the oxygen atoms has been obtained from space considerations. The point positions are:

3Hg in $3(a)$:$x0\frac{1}{3}$, $0x\frac{2}{3}$, $\bar{x}\bar{x}0$ with $x = 0.745$
3O in $3(b)$:$x0\frac{5}{6}$, $0x\frac{1}{6}$, $\bar{x}\bar{x}\frac{1}{2}$ with $x = 0.46$

This structure is built up of infinite spiral chains -O-Hg-O- running parallel to the c axis of the hexagonal unit cell. The distances and angles within the chains are:

Hg-O 2.03 Å The angle Hg-O-Hg 109°
Hg-Hg 3.30 Å The angle O-Hg-O 180°

This atomic arrangement is isostructural with the hexagonal modification of mercury(II)sulphide (cinnabar)[2]. The Hg-O distance and the bond angles are identical with those found in the planar zigzag chains -O-Hg-O- in orthorhombic mercury(II)oxide [3].

This investigation is to be continued by means of neutron diffraction methods in order to investigate the proposed oxygen arrangement. Studies on the stability relations between the modifications of mercury(II)oxide are in progress.

Hg_2O_2NaI. Space group $P6_222$ No. 180. Unit cell dimensions $a = 6.667$ Å, $c = 10.054$ Å. Cell content 3 formula units of Hg_2O_2NaI.

The positions of the mercury and iodine atoms have been derived on the basis of single crystal data.

6 Hg in $6(f)$:$\frac{1}{2}0z\frac{2}{3}, 0\frac{1}{2}\frac{2}{3}+z, \frac{1}{2}\frac{1}{2}\frac{1}{3}+z$
$\frac{1}{2}0\bar{z}, 0\frac{1}{2}\frac{2}{3}-z, \frac{1}{2}\frac{1}{2}\frac{1}{3}-z$ with $z=\frac{1}{3}$
3 I in $3(c)$:$\frac{1}{2}00, 0\frac{1}{2}\frac{2}{3}, \quad \frac{1}{2}\frac{1}{2}\frac{1}{3}$

This investigation is being continued in order to find the positions of the sodium and oxygen atoms.

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1. Laruelle, M. P. *Compt. rend.* **241** (1955) 802.
2. Aurivillius, K. *Acta Chem. Scand.* **4** (1950) 1413.
3. Aurivillius, K. *Acta Chem. Scand.* **10** (1956) 852.

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