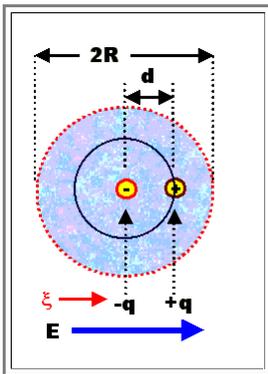## 3.2.2 Electronic Polarization

For calculating the effect of **electronic polarization**, We consider an idealized atom with *perfect **spherical symmetry***.

- It has a point like charge **+ ze** in the nucleus, and
- The exact opposite charge **– ze** homogeneously distributed in the volume of the atom, which is

$$V = \frac{4}{3}\pi R^3$$

- With **R =** radius of the atom

The charge density ρ of the electrons then is

$$\rho = -\frac{3z \cdot e}{4\pi \cdot R^3}$$

In an electrical field **E** a force **F_1** acts on charges given by

$$F_1 = z \cdot e \cdot E$$

- We will now drop the underlining for vectors and the mauve color for the electrical field strength **E** for easier readability.

The positive charge in the nucleus and the center of the negative charges from the electron "cloud" will thus experience forces in different direction and will become separated. We have the idealized situation shown in the image above.

The separation distance **d** will have a finite value because the separating force of the external field is exactly balanced by the attractive force between the centers of charge at the distance **d**.

- How large is his attractive force? It is not obvious because we have to take into account the attraction between a *point* charge and *homogeneously distributed* charge.
- The problem is exactly analogous to the classical mechanical problem of a body with mass **m** falling through a hypothetical hole going all the way from one side of the globe to the other.
- We know the solution to that problem: The attractive force between the point mass and the earth is equal to the attractive force between two point masses if one takes *only* the mass of the volume inside the sphere given by the distance between the center of the spread-out mass and the position of the point mass.
- Knowing electrostatics, it is even easier to see why this is so. We may divide the force on a charged particles on any place inside a homogeneously charged sphere into the force from the "*inside*" sphere and the force from the hollow "*outside*" sphere. Electrostatics teaches us, that a sphere charged on the outside has *no field* in the *inside*, and therefore *no force* (the principle behind a Faraday cage). Thus we indeed only have to consider the "charge *inside* the sphere.

For our problem, the attractive force **F_2** thus is given by

$$F_2 = \frac{q(\text{Nucleus}) \cdot q(e \text{ in } d)}{4\pi \epsilon_0 \cdot d^2}$$

- with **q(Nucleus) = ze** and **q(e in d)** = the fraction of the charge of the electrons contained in the sphere with radius **d**, which is just the relation of the volume of the sphere with radius **d** to the *total* volume . We have

$$q(e \text{ in } d) = ze \cdot \frac{(4/3) \pi \cdot d^3}{(4/3) \pi \cdot R^3} = \frac{ze \cdot d^3}{R^3}$$

🔵 and obtain for F_2:

$$F_2 = \left(\frac{(ze)^2}{4 \pi \epsilon_0 \cdot R^3} \right) \cdot d$$

◤ We have a linear force law akin to a spring; the expression in brackets is the "spring constant". Equating F_1 with F_2 gives the equilibrium distance d_E.

$$d_E = \frac{4 \pi \epsilon_0 \cdot R^3 \cdot E}{ze}$$

◤ Now we can calculate the **induced dipole moment** μ, it is

$$\mu = ze \cdot d_E = 4 \pi \epsilon_0 \cdot R^3 \cdot E$$

◤ The polarization P finally is given by multiplying with N, the density of the dipoles; we obtain

$$P = 4 \pi \cdot N \cdot \epsilon_0 \cdot R^3 \cdot E$$

🔵 Using the definition $P = \epsilon_0 \cdot \chi \cdot E$ we obtain the *dielectric susceptibility resulting from atomic polarization*, χ_{atom}

$$\chi_{atom} = 4 \pi \cdot N \cdot R^3$$

◤ Let's get an idea about the numbers involved by doing a simple exercise:

Exercise 3.2-3
Some numbers for atomic polarization

◤ This is our first basic result concerning the polarization of a material and its resulting susceptibility. There are a number of interesting points:

🔵 We justified the "law" of a linear relationship between E and P for the electronic polarization mechanism (sometimes also called atomic polarization).

🔵 We can easily extend the result to a mixture of different atoms: All we have to do is to sum over the relative densities of each kind of atom.

🔵 We can easily get an order of magnitude for χ. Taking a typical density of $N \approx 3 \cdot 10^{19} \text{ cm}^{-3}$ and $R \approx 6 \cdot 10^{-9} \text{ cm}$, we obtain

$$\chi \approx 8{,}14 \cdot 10^{-5}, \quad \text{or}$$
$$\epsilon_r = 1,000\,0814$$

◤ In words: the electronic polarization of *spherical* atoms, while existent, is *extremely weak*. The difference to vacuum is at best in the promille range.

◤ Concluding now that electronic polarization is totally unimportant, would be *premature*, however. Atoms in crystals or in any solids do not generally have *spherical* symmetry. Consider **the sp^3** orbital of **Si**, **Ge** or diamond.

🔵 Without a field, the center of the negative charge of the electron orbitals will still coincide with the core, but an external field breaks that symmetry, producing a dipole momentum.

🔵 The effect can be *large* compared to spherical **s**-orbitals: **Si** has a dielectric constant (**DK**) of **12**, which comes exclusively from electronic polarization! Some values for semiconductors are given in the link.

Questionaire

Multiple Choice questions to 3.2.2