A semi empirical calculation

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Abstract. A method has been developed for calculating radial wave functions by numerical integration of the Dirac equation. These wave functions are then used to obtain oscillator strengths. The idea is to use a one-electron radial symmetric potential gained from a modified Thomas-Fermi ionic charge distribution. The potential is produced by the core protons and the inner electrons. This charge cloud can be described by an effective core charge and is scaled in order to match the binding-energy of this 'one-electron' system with the experimental ionisation potential.

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1. Thomas-Fermi model

The aim of my diploma thesis is to calculate oscillator strengths which are (in first order perturbation theory) directly connected to the radial matrix element:

$$| < \psi_{nlj}| \; \boldsymbol{r} \; |\psi_{n'l'j'} > |^2 = \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \tag{1}$$

Therefore one needs to solve the Dirac equation in order to retrieve the correct radial wave function:

$$P_{nl}(r) = \begin{pmatrix} F(r) \\ G(r) \end{pmatrix} \tag{2}$$

In earlier publications (Bates & Damgaard 1949, Seaton 1958) only the asymptotic behaviour of the wave function in the outer parts (large r) was taken into account. This is improved using the complete solution of the Dirac equation. Therefore the potential energy of the ion has to be approximated in a realistic way. This is going to be achieved using the Thomas-Fermi atom model:

A single electron is expected to move in the central field produced by the remaining $\mathrm{N_e} - 1$ inner electrons and the $\mathrm{Z_{core}}$ core protons:

$$\mathrm{V}(r) = \begin{cases} \dfrac{\mathrm{Z_{core}} e_0}{r}, & r \to 0 \\ \dfrac{\mathrm{Z_{rest}} e_0}{r}, & r \geq r_0 \end{cases} \tag{3}$$

($\mathrm{Z_{rest}} = \mathrm{Z_{core}} - (\mathrm{N_e} - 1)$ the rest charge where $\mathrm{N_e}$ is the total number of electrons.)

If we treat the $\mathrm{N_e} - 1$ electrons as a free, degenerate electron gas at the temperature of zero Kelvin the potential of this continuous "charge cloud" can be calculated with quantum statistical methods and is described in a haviour of the potential can be quantified using an effective core charge:

$$V(r) \stackrel{!}{=} \frac{\mathrm{Z_{eff}}(r) e_0}{r} \tag{4}$$

This charge distribution function $Z_{\mathrm{eff}}(r)$ can be directly connected to the Thomas-Fermi function $\phi(r)$ which calculation is a problem that can only be solved numerical and is discussed in the thesis, too.

2. Dirac equation

Now that we have an expression for the potential (based on quantum statistics) the Dirac equations are given as follows:

$$\begin{aligned} \left(\frac{d}{dr} - \frac{\kappa}{r}\right) F(r) &= \left(\frac{mc}{\hbar}\left(1 - \frac{E}{E_0}\right) - \frac{\alpha Z_{\mathrm{eff}}(r)}{r}\right) G(r) \\ \left(\frac{d}{dr} + \frac{\kappa}{r}\right) G(r) &= \left(\frac{mc}{\hbar}\left(1 + \frac{E}{E_0}\right) + \frac{\alpha Z_{\mathrm{eff}}(r)}{r}\right) F(r) \end{aligned}$$

where:

$$\kappa = \begin{cases} -(l+1) & \text{f"ur } j = l + \frac{1}{2} \\ l & \text{f"ur } j = l - \frac{1}{2} \end{cases}, \quad E = E_{nj} + mc^2$$

The energy E of this electron system is fixed: the experimental determined value is used; the scaling factor α is varied instead which means that the potential is adjusted in order to reproduce the correct energy level. The solution of this coupled differential equations is achieved numerical. In the outer parts of the atom (for large r) it is possible to derive analytical solutions which are then matched to wave functions based on an outward integration started at the origin. This again is a separate part of the thesis: a power law expansion ansatz has to be used for achieving the correct behaviour near the origin. This analytical solutions are then used as starting points for the Runge-Kutta-Merson integration scheme.

3. Discussion

A semi empirical method for calculating oscillator strengths under the assumption of a spherical symmetric charge distribution has been introduced. This procedure for computing radial wave functions using the Dirac equations works best for atoms with alkali-like configuration: one electron moves in the (central) field produced by the core and the inner electrons just as can be found for e.g. $\mathrm{C_{IV}}$, $\mathrm{N_V}$ and $\mathrm{O_{VI}}$.

References

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