Bound states contribution to the polarizability of hydrogen

The polarizability α of hydrogen (with spin ignored) is given by the following expression (eq. 5.1.68 in Sakurai & Napolitano with $E_1 = -e^2/(2a_0)$ and $E_n = E_1/n^2$)

$$\alpha = 4a_0 \sum_{n=2}^{\infty} \frac{|\langle np_0|z|1s\rangle|^2}{1-n^{-2}} + \text{contribution from continuum states.} \tag{1}$$

We want to compute the matrix elements $\langle np_0|z|1s\rangle$ and then sum the series.

1 Wave functions

The wave functions of the hydrogen atom are

$$\psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta,\phi), \tag{1}$$

where the radial wave functions are

$$R_{nl}(r) = \frac{2}{n^2\, a_0^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}\, e^{-\rho/2}\, \rho^l\, L_{n-l-1}^{2l+1}(\rho) \tag{2}$$

where $\rho = (2r)/(na_0)$ and a_0 is the Bohr radius. In this formula, the associated Laguerre polynomials $L_n^m(x)$ are normalized as in Mathematica, Abramowitz & Stegun, and Gradshteyn & Ryzhik, while Griffiths uses the normalization $L_n^m(x)|_{\text{Griffiths}} = (n+m)!\, L_n^m(x)$, and Sakurai, Sakurai & Napolitano, Landau & Lifshitz use the normalization $L_n^m(x)|_{\text{Landau}} = (-1)^m n!\, L_{n-m}^m(x)$.

2 Matrix elements

We have

$$\begin{aligned}
\langle np_0|z|1s\rangle &= \langle n10|z|100\rangle && (1)\\
&= \int dr\, r^2\, d\Omega\, \psi_{n10}^*(r,\theta,\phi)\, z\, \psi_{100}(r,\theta,\phi) && (2)\\
&= \int dr\, r^2\, d\Omega\, R_{n1}(r) Y_{10}^*(\theta,\phi)\, z\, R_{10}(r)\, Y_{00}(\theta,\phi) && (3)\\
&= \int dr\, r^3\, d\Omega\, Y_{10}^*(\theta,\phi) \sqrt{\frac{4\pi}{3}}\, Y_{10}(\theta,\phi)\, R_{10}(r)\, \frac{1}{\sqrt{4\pi}} && (4)\\
&= \frac{1}{\sqrt{3}} \int dr\, r^3 d\Omega\, R_{n1}(r)\, Y_{10}^*(\theta,\phi)\, Y_{10}(\theta,\phi)\, R_{10}(r) && (5)\\
&= \frac{1}{\sqrt{3}} \int_0^\infty dr\, r^3\, R_{n1}(r)\, R_{10}(r). && (6)
\end{aligned}$$

We now pass to dimensionless form by defining x and $\tilde{R}_{nl}(x)$ as

$$\begin{aligned}
r &= x\, a_0, && (7)\\
R_{nl}(r) &= a_0^{-3/2}\, \widetilde{R}_{nl}(x). && (8)
\end{aligned}$$

Then

$$\langle np_0|z|1s\rangle = a_0\, b_n \tag{9}$$

with

$$b_n = \frac{1}{\sqrt{3}} \int_0^\infty dx\, x^3\, \widetilde{R}_{n1}(x)\, \widetilde{R}_{10}(x). \tag{10}$$

We evaluate b_n.

From Eq. (2) we compute

$$\widetilde{R}_{10}(x) = 2e^{-x}, \tag{11}$$

$$\widetilde{R}_{n1}(x) = \frac{4}{\sqrt{n^7(n^2-1)}}\, e^{-x/n}\, x\, L^3_{n-2}\big(\tfrac{2x}{n}\big). \tag{12}$$

Then

$$b_n = \frac{8}{\sqrt{3n^7(n^2-1)}} \int_0^\infty e^{-(1+\frac{1}{n})x}\, x^4\, L^3_{n-2}\big(\tfrac{2x}{n}\big)\, dx, \tag{13}$$

and with $x = nt/2$,

$$= \frac{1}{4\sqrt{3}} \sqrt{\frac{n^3}{n^2-1}} \int_0^\infty e^{-(n+1)t/2}\, t^4\, L^3_{n-2}(t)\, dt. \tag{14}$$

Now, formula 7.424.7 in Gradshteyn and Ryzhik gives

$$\int_0^\infty e^{-st} t^\beta L_n^\alpha(t) = \frac{\Gamma(\beta+1)\Gamma(\alpha+n+1)}{n!\Gamma(\alpha+1)} s^{-\beta-1} F(-n,\beta+1;\alpha+1;s^{-1}), \tag{15}$$

valid for $\mathrm{Re}\,\beta > -1$, $\mathrm{Re}\,s > 0$. Identifying $s \to (n+1)/2$, $\beta \to 4$, $n \to n-2$, $\alpha \to 3$, we find

$$\int_0^\infty e^{-(n+1)t/2}\, t^4\, L^3_{n-2}(t)\, dt = 64n^2(n-1)^{n-2}(n+1)^{-n-2}. \tag{16}$$

Finally

$$b_n = \frac{16n}{\sqrt{3}} \left(\frac{n}{n^2-1}\right)^{5/2} \left(\frac{n-1}{n+1}\right)^n. \tag{17}$$

Some values are

$$b_2 = \sqrt{2}\frac{2^7}{3^5}, \quad b_3 = \sqrt{2}\frac{3^3}{2^7}, \quad b_4 = \sqrt{5}\frac{2^{11}3}{5^7}, \quad b_5 = \sqrt{10}\frac{2\,5^3}{3^8}. \tag{18}$$

3 Summation over bound states

We have

$$\alpha = c\, a_0^3 \tag{1}$$

with

$$c = 4\sum_{n=2}^\infty \frac{b_n^2}{1-n^{-2}} + \text{contribution from continuum states.} \tag{2}$$

Including only the contribution from bound states, we want to evaluate

$$c = \sum_{n=2}^{\infty} c_n \quad \text{with} \quad c_n = \frac{4b_n^2}{1 - n^{-2}}. \tag{3}$$

This series converges because at large n, we have $b_n \sim n^{-3/2}$ and $c_n \sim n^{-3}$. To evaluate the sum, we add the first K terms and approximate the sum of the others with an Euler-Maclaurin series (dropping the derivative terms),

$$c \simeq \sum_{n=2}^{K} c_n + \frac{c_K}{2} + \int_K^{\infty} c_n \, dn. \tag{4}$$

With $K = 10$, this gives

$$c = 3.66309. \tag{5}$$

Thus we find

$$\alpha = 3.66309 \, a_0^3 \tag{6}$$

for the bound state contribution to the polarizability of a hydrogen atom in the ground state.

References

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