Error Analysis for the C_6 Coefficient in Rb.

The dispersion coefficient C_6 is expressed as an integral over the dynamic polarizability $\alpha(i\omega)$ through the equation

$$C_6 = \frac{3}{\pi}\int_0^\infty [\alpha(i\omega)]^2 \ . \tag{1}$$

The dynamic polarizability $\alpha(i\omega)$ is, in turn, given by

$$\alpha(i\omega) = \frac{2}{3}\sum_k \frac{(E_k - E_v)}{(E_k - E_v)^2 + \omega^2}\ \langle v|\vec{R}|k\rangle \cdot \langle k|\vec{R}|v\rangle \ , \tag{2}$$

where $|v\rangle$ is the valence state and $|k\rangle$ ranges over all excited states that can couple to the valence state through the dipole operator. Possible states $|k\rangle$ for an atom with one valence electron include excited valence states, states with two valence electrons and one core hole, states with three valence electrons and two core holes, and so forth.

We decompose the polarizability into three parts:

$$\alpha = \alpha_v + \alpha_c + \alpha_{vc} \ , \tag{3}$$

The term α_v, which is the contribution to Eq. (2) from valence excited states $|k\rangle$ only, is the dominant contribution for small values of ω. This term accounts for about 97% of $\alpha(0)$ for Rb. The terms $\alpha_c + \alpha_{vc}$ are the contributions to Eq. (2) from core hole states; these terms contribute the remaining 3%. The term α_c is the polarizability of the Rb^+ core, and α_{vc} is a counter term that compensates for Pauli-principle violating excitations in α_c.

(1) The contribution from excited valence states α_v can be reduced to the form:

$$\alpha_v(i\omega) = \frac{1}{3}\sum_k \frac{E_k - E_v}{(E_k - E_v)^2 + \omega^2}\langle v\|r\|k\rangle^2 \tag{4}$$

In the case of Rb, $v = 5s_{1/2}$ is the ground state and $k = np_{1/2}$ or $np_{3/2}$ are the possible excited valence states. The largest contributions to $\alpha_v(0)$ (>99%) are from the $5p_{1/2}$ and $5p_{3/2}$ states. For these states, we use *experimental* rather than theoretical reduced matrix elements and energies. The theoretical reduced matrix elements for these two transitions are accurate to about 0.5%, whereas the experimental reduced matrix elements are known to higher accuracy for the $5s - 5p$

Table 1: Theoretical and experimental dipole matrix elements (a.u.) in Rb.

	Theory	Ref. [1]	Ref [2]	Ref [3]	Expt.
$\langle 5p_{1/2}\|r\|5s\rangle$	4.221	4.231(3)	4.228(5)	4.236(3)	4.233(2)
$\langle 5p_{3/2}\|r\|5s\rangle$	5.956	5.977(4)	5.979(7)	5.983(10)	5.978(3)

transitions in Rb. The input data that we use for reduced matrix elements are shown in Table 1. The values in the column headed "Expt." are least-squares averages of the experimental values. In assessing the accuracy of this largest contribution, we use the experimental errors as discussed later.

(2) For np states with $n = 6 \cdots 8$, we use the *ab-initio* calculations of the $5s - np$ matrix elements given in Ref. [4], which are expected to be accurate to better than 5% based on comparisons of similar calculations with accurate experimental data in Cs. We also use experimental energies in this term.

(3) The contribution of np states with $n > 9$ to $\alpha_v(0)$ is very small (0.04%) and is evaluated in the Hartree-Fock approximation. We estimate the error in this term to be $< 50\%$ based on comparisons of HF and all-order calculations of the $5s - 8p$ contributions to α_v.

(4) To determine α_c, which contributes 3% to $\alpha(0)$, we use a theoretical value calculated in the random-phase approximation (RPA). To assess the accuracy of the RPA calculation for the Rb^+ core, we carry out a similar calculation for Kr and compare with benchmark theoretical calculations from Ref. [5]. We find for Kr, $\alpha(0) = 16.48$ and $C_6 = 127.2$ in the RPA, compared with the benchmark values $\alpha(0) = 17.06$ and $C_6 = 132.9$ from [5]. Our calculations of the core contributions to $\alpha(0)$ and C_6 for Kr are therefore about 4% too small. The Thomas-Reiche-Kuhn oscillator strength sum rule is satisfied exactly by RPA, so our value of $\alpha(i\omega)$ is exact in the large ω limit. Since the calculation of the polarizability of Rb^+ is formally identical to that for Kr, but less sensitive to correlation because of the higher nuclear charge, we estimate the error in α_c to be less than 4%.

(5) The term α_{vc}, which contributes 0.08% to $\alpha_v(0)$, is calculated in the

HF approximation and assigned an error of 50% using the considerations stated in item (3) above.

In our numerical program, we separate $\alpha(i\omega)$ in C_6 into five parts:

$$\alpha(i\omega) = \sum_{\lambda=1}^{5} \alpha_\lambda(i\omega)$$

The terms α_λ are:

α_1 is the contribution to α_v from the $5s - 5p_{1/2}$ transition. Its uncertainty is governed by the uncertainty in the *experimental* value of the $\langle 5s\|r\|5p_{1/2}\rangle$ matrix element. The relative error in the matrix element $\sigma = 0.00046$ and the relative error in α_1 is 0.00092.

α_2 is the contribution to α_v from the $5s - 5p_{3/2}$ transition. Its uncertainty is governed by the uncertainty in the *experimental* value of the $\langle 5s\|r\|5p_{3/2}\rangle$ matrix element.The relative error in the matrix element $\sigma = 0.00055$ and the relative error in α_2 is 0.00110.

α_3 is the contribution to α_v from the $5s - np_{1/2}$ and $5s - np_{3/2}$ transitions with $n = 6,\ 7,\ 8$. Its uncertainty is governed by the uncertainty in the all-order theoretical values of the $\langle 5s\|r\|np_j\rangle$ matrix elements. The relative error of these matrix elements is assumed to 5%; the corresponding relative error in α_3 is 0.1 .

α_4 is the RPA value of α_c. Its relative error is taken to be 0.04 based on the comparison of a similar RPA calculation with benchmark values for Kr.

α_5 is the sum of the HF value of α_{vc} and the HF value of the contributions to α_v from states with $n > 9$. Its relative error is taken to be 0.5 based on the comparison of a HF and all-order calculation of the $5s - 8p$ contribution to α_v.

We evaluate the change in C_6 induced by each of these individual sources using

$$\delta_\lambda C_6 = 2\ [C_6]_\lambda\ r_\lambda\ ,$$

where r_λ is the relative error in α_λ, and

$$[C_6]_\lambda = \frac{3}{\pi}\int_0^\infty d\omega\ \alpha(i\omega)\ \alpha_\lambda(i\omega)\ .$$

Table 2: Contributions to C_6 and δC_6 for Rb.

λ	C_6	$\delta C_6(1\sigma)$	$\delta C_6(2\sigma)$	$\delta C_6(3\sigma)$
1	1473	2.7	5.4	8.1
2	2912	6.4	12.8	19.2
3	27	5.4	5.4	5.4
4	286	22.9	22.9	22.9
5	-5	-5.0	-5.0	-5.0
Tot	4693	25.0	27.8	31.8

We use the square root of the sum of squares of $\delta_\lambda C_6$ as the error in C_6. It should be noted that

$$C_6 = \sum_{\lambda=1}^{5} [C_6]_\lambda \ .$$

The contributions to C_6 from the five terms above, and the associated uncertainties are listed in Table 2. We list columns with 1σ, 2σ, and 3σ values for the uncertainties in the experimental matrix elements. In the last row, we give our final value for C_6 together with error estimates based on three assumptions concerning the errors in the experimental data used to evaluate the dominant terms α_1 and α_2. Our best estimate of the value is $C_6 = 4693 \pm 25$. This value can be compared with the value $C_6 = 4691 \pm 23$ given in Ref. [6]. The reason for the small differences is that two different RPA calculations were used for $\alpha_c(i\omega)$; the present value is from a non-relativistic RPA calculation, whereas the one value used in [6] is from a relativistic RPA calculation. A more conservative estimate, based on 3σ errors in the two experimental matrix elements, is $C_6 = 4693 \pm 32$.

References

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