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Hartree–Fock Third-Harmonic Coefficient of Neon

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This is a note concerned with a previous publication by R. Klingbeil, V. G. Kaveeshwar, and R. P. Hurst [Phys. Rev. A 4, 1760 (1971)] giving specific results for neon.

Recently Klingbeil, Kaveeshwar, and Hurst[1] (KKH) derived the Hartree–Fock expression for the third-harmonic coefficient (THC) of an atomic system by a method employing Chung's time-dependent perturbation theory.[2] KKH also obtained the Hartree–Fock THC (HFTHC) of helium. It is the purpose of this note to present the results of a calculation of the HFTHC of neon.

It is necessary to obtain zeroth-, first-, and second-order wave functions in order to evaluate the expression for the THC given by Eq. (17) of KKH. The zeroth-order wave function chosen is that of Clementi.[3] First-order wave functions are obtained by the method of Kaveeshwar, Chung, and Hurst,[4] and agreement with their calculation of the linear dynamic polarizability is excellent. Second-order wave functions are obtained by the method of KKH.

The results of the calculation of the HFTHC $X_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega)$ of neon are presented in Table I and plotted in Fig. 1 along with the HFTHC of helium[1] for comparison. At zero frequency the HFTHC of neon is 54.0 a.u. Surprisingly, this result is significantly larger than the Hartree–Fock static hyperpolarizability result of 42 a.u. obtained by Sitter and Hurst.[5] Both results are considerably below the experimental static hyperpolarizability

TABLE I. Hartree–Fock third-harmonic coefficient of neon.

ω (a.u.)	λ(Å)	$\chi_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega)$ (a.u.)
0.000	∞	54.0[a]
0.025	18 238	54.9
0.050	9119	57.9
0.075	6079	63.2
0.100	4559	72.0
0.125	3648	86.1
0.150	3040	109.6
0.175	2605	152.5
0.200	2280	246.7
0.225	2026	570.6
0.247	1846[b]	100 939.1
0.248	1838	−16 333.3

[a] $\chi_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega) = 54.0$ a.u. at zero frequency.
[b] $\frac{1}{3}(1846\ \text{Å}) = 615\ \text{Å}$ is the calculated value of the first transition wavelength. The experimental value is 736 Å.

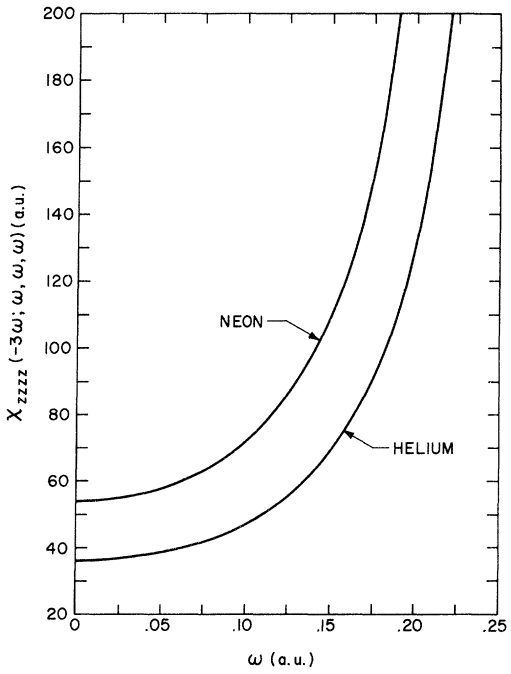

FIG. 1. Hartree–Fock third-harmonic coefficient $\chi_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega)$ of helium (Ref. 1) and neon (this work).

result of ~ 100 a.u. obtained by a method employing the Kerr effect.[6]

Ward and New[7] obtained the THC's of helium, neon, and other gases using a ruby-laser light beam with a wavelength $\lambda = 6943$ Å. Their result for the THC of neon is 106 a.u., which is obtained by scaling measurements to the calculation of the THC of helium presented by Sitz and Yaris.[8] Sitz and Yaris use time-ordered time-dependent perturbation theory and determine that the THC of helium at $\lambda = 6943$ Å is 47.7 a.u. with an estimated accuracy of 1%. At 6943 Å the HFTCH's of helium and neon are 40.2 and 60.9 a.u., respectively. The neon result is very far below the experimental value.

The ratio of the measured THC of neon to helium is $\frac{106}{47.7} = 2.2$ and the HFTHC ratio is $\frac{60.9}{40.2} = 1.5$. This discrepancy is somewhat disappointing since it indicates that the HFTHC results do not scale well and may therefore be a poor indication of experimental results.

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Is There a Need to Calculate Positronium and Muonium hfs to Higher Order?

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An estimate of $\alpha^4 R_\infty$ contributions to positronium and muonium hfs is made in somewhat greater detail than heretofore. Comparison with the most recent experimental data suggests that such additional corrections could well improve agreement between theory and experiment. Indeed, the one immediately calculable $\alpha^4 R_\infty$ contribution almost totally accounts for present discrepancies.

The present comment is motivated by the most recent value obtained for the ground-state triplet-singlet splitting of positronium,[1] which is stated in Ref. 1 to differ from the most recent theoretical value[2] by six standard deviations. The theoretical contribution[2] in order[3] $\alpha^4 \ln\alpha^{-1} R_\infty$ is + 34 MHz. The discrepancy between theory and experiment is -23 ± 4 MHz. The questions I propose to raise are whether this discrepancy could be accounted for by the hitherto uncalculated contributions of order $\alpha^4 R_\infty$ and whether such contributions would be consistent with the experimental results for muonium hfs. The answer to both questions appears to be yes and points up the need of extending hfs calculations to higher order for both of these atoms.

In order to obtain my estimates of uncalculated terms, it is convenient to separate contributions to $\nu_{\rm hfs}$ into three parts:

$$\nu_{\rm hfs} = C(r)[Q + A + rR(r)] \,. \tag{1}$$

The quantities appearing in Eq. (1) are defined as follows:

$$C(r) = \tfrac{8}{3}(1+r)^{-3}, \quad r = m_-/m_+ \,, \tag{2}$$

where m_- is the mass of the electron, m_+ the mass of the positron or μ_+ meson, respectively. The term Q is the standard quantum-electrodynamical (QED) correction without recoil terms, which also occurs for hydrogen. It is

$$Q = 2\alpha^2 R_\infty (\mu_+/\mu_B)\{1 + a_e + \alpha^2[9/4 + c_l(-13/4 + \ln 2)] + O(\alpha^3 \ln^2 \alpha^{-1})\} \,, \tag{3}$$

with $c_e = 2$, for positronium, and $c_\mu = c_H = 1$ for muonium and hydrogen.[4] The term a_e is the anomalous magnetic moment of the electron:

$$a_e = \tfrac{1}{2}\frac{\alpha}{\pi} - 0.3285\left(\frac{\alpha}{\pi}\right)^2 + O(\alpha^3) \,. \tag{4}$$

For positronium, we have

$$(\mu_+/\mu_B) = 1 + a_e \,, \tag{5}$$

and for muonium, the observed magnetic moment