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Brief Reports

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Hyperpolarizability of the neon atom

M. Jaszuński* and D. L. Yeager
Department of Chemistry, Texas A&M University, College Station, Texas 77843

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The multiconfiguration time-dependent Hartree-Fock method is applied to compute the hyperpolarizabiltiy of the neon atom and its frequency dependence. For the static limit $\gamma = \gamma(0;0,0,0)$ we obtain $\gamma = 86.5$ a.u. This value agrees very well with a recent experimental value of 75 a.u. $< \gamma < 93$ a.u. obtained by Shelton and Lu [Phys. Rev. A **37**, 3813 (1988)]. The results for the Kerr hyperpolarizability $\gamma(\omega;0,0,\omega) = \gamma^{\text{Kerr}}$ provide an estimate of the dispersion effects. Approximating our results with the formula $\gamma^{\text{Kerr}} = \gamma(1 + A\omega_L^2)$, where for the Kerr effect $\omega_L^2 = 2\omega^2$, we find $A \approx 0.50 \times 10^{-10}$ cm^2.

The hyperpolarizability of the Ne atom has been recently studied theoretically[1] and experimentally.[2,3] Unfortunately, the results of these studies cannot be directly compared, as the experimental data were obtained from an electric-field-induced second-harmonic generation (ESHG) experiment, whereas the calculations have been performed for the static hyperpolarizability. In this Brief Report, we attempt to complement these results and provide new *ab initio* results for $\gamma(-\omega;0,0,\omega)$, the dc Kerr hyperpolarizability of Ne, including $\gamma(0;0,0,0)$—the static limit.

For the calculations of the polarizability we perform, we utilize the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method.[4-6] The MCTDHF method yields the correct linear-response equations for the multiconfiguration self-consistent-field (MCSCF) wave function. Other techniques using alternative multiconfigurational wave functions, such as many-body perturbation theory (MBPT), coupled-cluster, and limited (not full) configuration-interaction (CI) methods, only approximate the correct linear response.[7] The MCTDHF method has been shown in numerous cases to provide a good approximation to the full CI limit,[8-10] although sometimes large active spaces have to be used.[10]

In contrast to standard finite-field methods, the MCTDHF method is, in addition, capable of yielding the frequency-dependent polarizabilities $\alpha(\omega)$. This is an important advantage of both TDHF and MCTDHF approaches, since it enables direct comparison of the computed polarizabilities with spectroscopic data from experiment (available for $\omega \neq 0$).

A simple technique to compute the nonlinear polarizabilities is obtained combining the finite-field perturbation method and the linear-response equations.[11] This method is extremely simple to program and use once a TDHF or MCTDHF program is available. It is based on the expansion[12]

$$\alpha^F(\omega) = \alpha^0(\omega) + K\gamma(-\omega;0,0,\omega)\cdot F^2 + \cdots , \qquad (1)$$

where $\alpha^F(\omega)$ is the frequency-dependent dipole polarizability in the presence of an additional static field F, K is a constant determined by the symmetry relations (α and γ are tensors, F is a vector), and the terms vanishing for an atom due to spherical symmetry have been omitted. In this work, in contrast to Ref. 11, higher numerical accuracy was used throughout the calculations and the higher-order terms in Eq. (1) were found to be negligible. Therefore, the equations practically solved were (for z direction of the field F)

$$\alpha_{xx}^F(\omega) = \alpha^0(\omega) + \tfrac{1}{2}\gamma_{xzzx}(-\omega;0,0,\omega)F_z^2 \qquad (2)$$

and

$$\alpha_{zz}^F(\omega) = \alpha^0(\omega) + \tfrac{1}{2}\gamma_{zzzz}(-\omega;0,0,\omega)F_z^2 . \qquad (3)$$

To obtain the Kerr hyperpolarizability, we thus performed two MCTDHF calculations. The first to determine $\alpha^0(\omega)$ was a standard linear-response calculation. In the second, instead of the original MCSCF function, a finite-field perturbed MCSCF wave function described the reference state. The following linear-response calculation provided $\alpha^F(\omega)$, and the hyperpolarizability components were determined from Eqs. (2) and (3) using numerical differentiation. These calculations are the first (to our knowledge) MCTDHF calculations for hyperpolarizabilities.

The MBPT study of Cernusak *et al.*[1] is the most accurate analysis of Ne polarizabilities previously published. We have used their carefully optimized (14.9.7.6/9.6.5.3) basis set consisting of 87 contracted Gaussian-type-orbital (CGTO) functions. At the self-consistent-field (SCF) level, we reproduce their results (obtained applying the finite-field perturbation technique), both for the dipole polarizability and for the static hyperpolarizability. We have used, as discussed above, a different and, in principle, highly accurate method [i.e., MCTDHF and Eqs. (1)–(3) above] to compute the correlation effects and to obtain the linear- and nonlinear-response properties.

The finite-field strength was chosen to be $F=0.01$ a.u. A test of the relative accuracy of our calculations is provided by a comparison of three values of $\gamma=\gamma_{zzzz}(0;0,0,0)$ obtained from (a) standard finite-field energy calculation; (b) $\alpha_{xx}^{F}(0)$ calculation, Eq. (2); and (c) $\alpha_{zz}^{F}(0)$ calculation, Eq. (3) [for the static hyperpolarizability of an atom $\gamma_{zzzz}(0;0,0,0)=3\gamma_{xzzx}(0;0,0,0)$]. For example, in the SCF (TDHF) approximation, we obtain 63.74, 63.55, and 63.61 a.u. (to be compared with 63.9 in Ref. 1). These differences are practically negligible, and presumably result from both numerical errors (10^{-10} a.u. error in energy results in changes of this magnitude in γ) and neglect of higher-order terms in F.

Our configuration expansion for the MCSF ground state included all the single, double, triple, and quadruple excitations from the $2s$ and $2p$ orbitals to $3s$ and $3p$ orbitals. Such an MCSCF wave function has been used recently[13] and gives for the linear-response (MCTDHF) static polarizability $\alpha=2.6185$ a.u. Our calculation, which employs a larger basis set, with the above choice of configurations gives $\alpha=2.6231$ a.u. for the linear-response static polarizability. This result is in very good agreement with both experiment—e.g., 2.669 a.u. in Ref. 14—and other theoretical values (see Ref. 1 for a discussion of previous results). The frequency dependence of the polarizability in our MCTDHF approximation is in good agreement with experimental values.[14] Similarly, the C_6 dispersion coefficient computed using the oscillator strengths, 6.277, compares well with the value based on experimental data, 6.352.[14]

For the static hyperpolarizability, our MCTDHF value is $\gamma=86.5$ a.u. This agrees very well with experimental result of Shelton and Lu,[2] 75 a.u. $<\gamma<93$ a.u. However, according to more recent measurements by Shelton[3] (which suggest a different extrapolation to zero frequency), γ is estimated to be ~ 113 a.u. Our value of γ is below the MBPT(4) result of Cernusak *et al.*[1] Unfortunately, their calculations, *as they noted,* have not reached convergence with perturbation order in MBPT—the results were 95.8 a.u. at MBPT(2), 80.5 a.u. at MBPT(3), and 104.6 a.u. at MBPT(4). Similar results have been obtained most recently by Maroulis and Thakkar.[15] Their SCF value of $\gamma(0)$ is $\sim 10\%$ larger, but their MBPT and coupled-cluster calculations yield results in the range 94.7–115.7 a.u. We note that both the MBPT and coupled-cluster calculations are based on a single principal configuration.

The frequency dependence of our results is conveniently discussed using the approximation proposed by Shelton:[16]

$$\gamma(\omega_0;\omega_1,\omega_2,\omega_3)=\gamma(0;0,0,0)(1+A\omega_L^2+B\omega_L^4)\ , \qquad (4)$$

where we ignore the higher-order terms in ω_L. For any optical process characterized by $\gamma(\omega_0;\omega_1,\omega_2,\omega_3)$ the frequency ω_L is defined as

$$\omega_L^2=\omega_0^2+\omega_1^2+\omega_2^2+\omega_3^2\ , \qquad (5)$$

and A and B are constant for a given atom or molecule. This approximation, which allows for an easy estimate of the frequency dependence of numerous hyperpolarizabilities once any one of them is known, has more recently been analyzed and explained from a theoretical viewpoint by Bishop.[17] In our case, we shall compare the ESHG experimental results for $\gamma(-2\omega;\omega,\omega,0)=\gamma^{\text{ESHG}}$ (when $\omega_L^2=6\omega^2$) with dc Kerr hyperpolarizabilities, $\gamma(-\omega;0,0,\omega)$ (in this case $\omega_L^2=2\omega^2$).

The initial value obtained by Shelton for A was $(1.78\pm0.34)\times10^{-10}$ cm^2, that is, ~ 8.57 a.u.$^{-2}$. We found that whatever approximation we use, our results are much smaller. We have tried fitting to Eq. (4) the MCTDHF results we have for $\gamma_{zzzz}(-\omega;0,0,\omega)$ and $\gamma_{xzzx}(-\omega;0,0,\omega)$, as well as the proper combination for the Kerr experiment, $\frac{3}{2}[\gamma_{zzzz}(-\omega;\omega,0,0)-\gamma_{xxzz}(-\omega;\omega,0,0)]$. In addition, we tried to include or neglect the ω_L^4 term, and we find all our results to be very much the same. The constant A is approximately 2.3 a.u.$^{-2}$, which is $\sim\frac{1}{4}$ of the first experimental estimate, when the ω_L^4 term is included, and B is ~ 5 a.u.^{4} (if $B\equiv0$, we find $A\sim2.4$ a.u.$^{-2}$). The new experimental data[3] indicate that the frequency dependence of the ratio $\gamma^{\text{ESHG}}(\text{Ne})/\gamma^{\text{ESHG}}(\text{He})$, and hence presumably also $\gamma^{\text{ESHG}}(\text{Ne})$, differs significantly from the initial estimates. Our results are in good agreement with previous, much more approximate calculations,[18,19] which have been done also for various other optical processes. Both coefficients, A and B, are only slightly larger (ca. 10–15 %) in the MCTDHF approximation than the corresponding TDHF results.

Further, very-large-scale *ab initio* studies of neon hyperpolarizabilities are certainly desirable. According to the results of Maroulis and Thakkar,[15] modification of the basis set may lead to an increase of γ^{SCF} of the order of $\sim 10\%$. This is in agreement with the numerical results of Voegel *et al.*,[20] available for γ^{SCF}. However, according to Ref. 1, this result "has a rather low numerical accuracy." Within the MCTDHF approximation, it might be useful to extend the number of active (partially occupied) orbitals. Our choice of the active space is satisfactory for the polarizability, but a larger active space may be needed for hyperpolarizability.

On the other hand, the calculated frequency dependence of the Kerr hyperpolarizability appears to be practically independent of correlation effects. It is also similar to the frequency dependence of γ(He). This suggests that the ratio of $\gamma(\text{Ne})/\gamma(\text{He})$ may be a nonlinear function of ω_L^2, in agreement with the new ESHG data.[3] A series of dc Kerr measurements at low frequency would undoubtedly be useful to definitively establish the neon-atom hyperpolarizability and its frequency dependence.

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[*] Permanent address: Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.

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