

PHYSICAL REVIEW LETTERS

VOLUME 28

29 MAY 1972

NUMBER 22

Coulomb Approximation for Analytic Multipole Polarizabilities of Ground- and Excited-State Atoms

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(Received 3 April 1972)

An analytic expression for the 2^l -pole static electric polarizability α_l of an atom is obtained in a Coulomb-like approximation. Core effects are neglected and, for simplicity, we consider only s -type valence electrons. Accurate values are obtained for the dipole and quadrupole polarizabilities of the alkali atoms and of four alkalilike excited states. Values close to those obtained from coupled Hartree-Fock calculations are computed for several divalent systems.

Atomic oscillator strengths have long been calculated from analytic, asymptotically correct wave functions.¹ Such functions, however, have not been extensively used to compute polarizabilities and dispersion forces. This is perhaps because there exist good semiempirical² and *ab initio*³ methods for obtaining these quantities. But for weakly bound anions, excited states, and higher multipoles, these methods are less successful. In just these cases, however, asymptotic wave functions should prove especially effective. This was shown previously for the hydride ion.^{4,5} In that work, an accurate analytic expression for the H^- dynamic polarizability was computed⁴ and then used to calculate the constants C_6 and C_8 .⁵

Here we compute an analytic expression (actually a rapidly "convergent" asymptotic series) for the polarizability of a neutral atom or positive ion in a Coulomb-like approximation. For simplicity, we assume that the atom has only s -type valence electrons. We also ignore the core contribution to the polarizability. To compute the 2^l -pole static electric polarizability we solve the equation

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{Z^2}{2\nu^2} + \frac{\lambda(\lambda+1) - l(l+1)}{2r^2} \right] \psi_l^{(1)}(\vec{r}) = r^l P_l(\cos\theta) \psi_\nu(r). \quad (1)$$

Here Z is the effective nuclear charge felt by a valence electron in the asymptotic region. The non-integral principal quantum number ν is determined from¹ $E = Z^2/2\nu^2$, where E is the experimental ionization energy of a valence electron. The effective angular-momentum quantum number λ is calculated from the equation $E_{nl} = Z^2/2(n+\lambda-l)^2$ which arises from solving the homogeneous eigenvalue problem⁶ related to Eq. (1). E_{nl} is the experimental ionization potential of the $(n-l)$ th state of l -type symmetry which is the state of that symmetry energetically closest to the state of interest. The valence orbital $\psi_\nu(r)$ is approximated by the properly normalized Whittaker function.¹ We have used an r^{-2} -type pseudopotential⁶ since Eq. (1) cannot be solved analytically with a more accurate potential. For N valence electrons, the polarizability is

$$\alpha_l = 2N \langle \psi_\nu | r^l P_l(\cos\theta) | \psi_l^{(1)} \rangle. \quad (2)$$

To solve Eq. (1), we employ the powerful Laplace-transform technique developed by Schwartz and Tiemann⁷ for treating perturbations on the hydrogen atom ($\lambda=l$, ν an integer). They showed that the

perturbation energy can be obtained without inverting the Laplace transform. This is very convenient for hydrogen and essential for the more complicated case treated here. Schwartz and Tiemann express the perturbation energy in terms of the solution of their transformed equation and its derivatives, all evaluated at a singular point of the transformed equation. Adapting their method to our problem, we find the polarizability can be expressed in terms of the transform function and its "nonintegral derivatives."⁸ These arise since λ and ν are nonintegral. To evaluate these quantities, we find a general expression for integral derivatives using the Schwartz-Tiemann procedure. Then we cast this expression into a form which can be used for nonintegers. This involves performing a sum whose upper limit is the order of the derivative.

The sum arising from the p th (integral) derivative is

$$\sigma(p) = \sum_{q=0}^p \frac{\Gamma(l+\lambda+2+q)\Gamma(l+\lambda+3+q)}{\Gamma(2\lambda+2+q)} \frac{\Gamma(\lambda-\nu+q+1)}{q! \Gamma(l+\lambda+3+q-\nu)}, \quad (3)$$

and the polarizability is expressible as the asymptotic series

$$\alpha_i = \frac{N}{Z} \left(\frac{\nu}{2Z} \right)^{2l+1} \frac{1}{2l+1} \sum_{k=0}^{\infty} (-1)^k \frac{\Gamma(\nu-k+l-\lambda+1)\Gamma(\lambda+l+\nu-k+2)\sigma(\nu-k+l-\lambda)}{k! \Gamma(\nu-k+l)\Gamma(\nu-k)\Gamma(l+2-k)}. \quad (4)$$

The series can be truncated at $k=l+1$ to four- or five-figure accuracy. Expanding the bracketed factor in Eq. (3) to first order in $\delta = \lambda - l$, we find

$$\sigma(p) = g(l+2, 2l+2, l+\nu-\lambda, 2l+2, 2l+2+p) + \delta g(l+2, 2l+1, l+\nu-\lambda-1, 2l+1, 2l+1+p), \quad (5)$$

where

$$g(i, j, x, L, U) = \sum_{r=L}^U \frac{r!}{(r-j)!} \frac{\Gamma(r-i-x+1)}{\Gamma(r-x+1)}. \quad (6)$$

The error from this expansion is $\sim 3\%$ for the worst case considered here (Cs, $l=2$, $\delta \approx -0.5$) and is $\ll 1\%$ for most of the other cases.⁹

The sum g is nonstandard but can be evaluated⁸ using summation methods from the calculus of finite differences. The result is

$$g(i, j, x, L, U) = G(U+1) - G(L),$$

where

$$G(r) = \frac{+j!}{(i-1)!} \left\{ - \frac{\Gamma(r+1)}{\Gamma(r-x)} \sum_{p=0}^{i-2} \frac{\Gamma(r-x-i+p+1)(i-p-2)!}{\Gamma(r+p-j+1)(j-p)!} \right. \\ \left. + \frac{1}{(j-i+1)!} \left[\frac{\Gamma(x+1)}{\Gamma(x+i-j)} \psi(r-x) + \sum_{m=1}^{j-i+1} S_{j-i+1}^{(m)} \sum_{k=1}^m \frac{x^{m-k} B_k(r)}{k} \right] \right\}, \quad (7)$$

TABLE I. Comparison of dipole polarizabilities (in \AA^3) calculated from Eq. (4) with previous work for alkali-like systems. The results of column 4 are calculated with the values of δ given in column 2. These are obtained from experimental energy levels (see text).

Atom	δ	Eq. (4) ($\delta=0$)	Eq. (4)	Ref. 11	Ref. 12 ^a	Ref. 2
Li ⁺ (2 ¹ S)	0.014	16.5	14.5	...	14.6	...
Li ⁺ (2 ³ S)	-0.053	5.55	7.06	...	6.95	...
He(2 ¹ S)	0.010	122.8	117.3	...	118.8	116.0
He(2 ³ S)	-0.062	40.6	47.2	...	46.8	46.4
Li	-0.032	23.3	24.6	...	24.7	24.4
Na	0.117	28.3	23.8	24.4 \pm 1.7	22.3	24.6
K	0.233	67.6	43.2	45.2 \pm 3.2	43.0	41.6
Rb	0.280	81.4	48.2	48.7 \pm 3.4	45.5	43.9
Cs	0.345	144.2	61.0	63.3 \pm 4.6	61.2	53.8

^aAlkali polarizabilities are from the work of Sternheimer, and the excited-state polarizabilities are from the highly accurate calculations of Chung and Hurst.

TABLE II. Comparison of quadrupole polarizabilities (in \AA^5) calculated from Eq. (4) with the results of Ref. 13 for alkali-like systems. The results of column 4 are calculated with values of δ given in column 2. These are obtained from experimental energy levels (see text).

Atom	δ	Eq. (4) ($\delta=0$)	Eq. (4)	Ref. 13
$\text{Li}^+(2^1\text{S})$	-0.002	6.89	6.89	...
$\text{Li}^+(2^3\text{S})$	-0.001	3.57	3.57	...
$\text{He}(2^1\text{S})$	-0.001	291.3	291.5	...
$\text{He}(2^3\text{S})$	-0.002	110.1	110.2	...
Li	0.027	59.5	58.8	60.0
Na	-0.010	74.4	74.8	74.8
K	-0.142	181.0	195.0	211.5
Rb	-0.233	212.6	253.2	261.4
Cs	-0.445	323.5	436.2	440.8

where $\psi(x)$ is the psi function,¹⁰ $S_j^{(m)}$ is a Stirling number of the first kind,¹⁰ and $B_k(r)$ is a Bernoulli polynomial.¹⁰

Combining Eqs. (7), (5), and (4), we have the desired expression for α_l . It has poles at $\nu = \lambda + n$ for integers $n \geq 1$. This correctly reflects the eigenvalue spectrum of our simple pseudopotential. Having these poles at the proper position is essential, and this is why we introduced $\lambda \neq l$. This is, of course, particularly true for excited states since if $\nu \geq l + 1$ the polarizability varies extremely rapidly with $\nu - \lambda$.

Dipole and quadrupole polarizabilities for certain alkali-like systems are presented in Tables I and II. Dipole polarizabilities for the case $\lambda = l$ (no pseudopotential) and for λ chosen as described above are compared in columns 3 and 4 of Table I. Columns 5, 6, and 7 give the results of previous experimental,¹¹ theoretical,¹² and semiempirical² work. Equation (4) gives results in good agreement with this representative sample of previous work.

In Table II we compare our quadrupole polarizabilities for these systems with Sternheimer's.¹³ Agreement is satisfactory. Notice that inclusion of the pseudopotential, though still necessary, is not as crucial as in the dipole case. This is because the first pole occurs at $\nu = 3 + \delta$ for α_2 while it occurs at $\nu = 2 + \delta$ for α_1 . Thus its precise position more strongly influences the dipole results.

In Table III we compare dipole polarizabilities for several divalent atoms and ions with previous work. The results for these distinctly non-Coulombic systems are only slightly poorer than those obtained from coupled Hartree-Fock (HF) calculations. Similar results are obtained for the quadrupole polarizabilities.⁸ The results present-

TABLE III. Comparison of dipole polarizabilities (in \AA^3) calculated from Eq. (4) with previous work for divalent systems.

Atom	Eq. (4)	Coupled HF ^a	Accurate
He	0.188	0.196 (0.196)	0.205 ^b
Li^+	0.0273	0.0280 (0.0281)	0.0285 ^b
Be^{++}	0.00753	0.00765	...
Be^{+++}	0.00285	0.00289	...
Be	6.02	6.75 (6.26)	6.93 ^c
B^+	1.86	1.68 (1.40)	...
Mg	10.5	12.0	11.1 \pm 0.5 ^d

^aUnbracketed numbers except for Mg are from H. D. Cohen, J. Chem. Phys. 43, 3558 (1965). Mg result is from S. Kaneko and S. Arai, J. Phys. Soc. Jap. 26, 170 (1969). Bracketed numbers are from Ref. 3.

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ed here indicate that Eq. (4) will give accurate polarizabilities for systems in Rydberg-like excited states, and will even provide a quick reasonable estimate for many systems which deviate significantly from Rydberg-like behavior. The accuracy of our approximation will improve within an isoelectronic sequence as Z and ν increase and will clearly deteriorate as the number of electrons significantly contributing to the polarizability increase. The success of Eq. (4) for helium ($Z=1$, $\nu \approx 0.75$) indicates that reasonable polarizabilities can be calculated from it for any divalent system.

Full account of this work with further applications will be presented shortly.⁸ In that paper we will also discuss difficulties with an earlier approach to this problem by Dalgarno and Pengelly.¹⁴ Extension to the frequency-dependent case and calculation of multipole dispersion forces is now in progress and generalization to other angular symmetries appears straightforward. It is also possible that two-photon absorption can be treated using our approach, but the calculation will undoubtedly be difficult.

We wish to thank Professor D. R. Herschbach and Professor Martin Karplus for their encouragement and support of this work. Support of the National Science Foundation is gratefully acknowledged.

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⁹We made these error estimates by calculating $\sigma(\nu - k + l - \lambda)$ for $\nu - \lambda$ an integer. For this case $\nu - k + l$

$-\lambda$ is an integer, and the result from Eq. (7) can be directly checked by simply adding up the terms in Eq. (3). For Rb ($l=2$, $\delta \approx -0.25$), $\nu - \lambda \approx$ an integer and we can verify that the error is only 0.5%. For the other systems, errors were estimated using the above procedure and interpolation.

¹⁰*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1966).

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Two-Photon Superradiance*

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(Received 2 April 1972)

A transient two-photon process is observed in the infrared which exhibits all the co-operative properties associated with superradiant two-level systems. It arises when a cw laser beam excites a molecular sample whose *level degeneracy* is suddenly removed by a Stark field. The resulting emission, which heterodynes with the laser, gives precise ground- and excited-state Stark splittings, and decays with a homogeneous relaxation time since Doppler dephasing effects are absent in forward scattering.

Superradiance¹ in the past has been associated exclusively with a one-photon process which produces coherent spontaneous emission in an ensemble of two-level systems. In this Letter, we extend the concept of superradiance to three levels which are connected by a two-photon transition and report a new coherent transient effect of this type. The effect arises when a molecular sample is excited by a cw laser beam and its level degeneracy is suddenly removed by a Stark field. The Stark-pulse technique also has led recently to the observation of photon echoes,² optical nutation,² and free-induction decay.³

As a point of reference, consider first a nondegenerate Doppler-broadened transition. We assume that initially the degeneracy is lifted by a constant Stark field and that under steady-state conditions only two of its levels are in resonance with a cw laser beam. Sudden application of a step-function Stark field switches these molecules out of resonance, and they emit an optical free-induction decay signal.³ This superradiant emission propagates in the forward direction, is collinear with the laser beam, and produces a heterodyne beat signal at a detector monitoring the

transmitted light. The beat appears as a damped oscillation whose frequency is the Stark shift. We note that the decay of this signal is due to (1) relaxation processes which determine the homogeneous linewidth, and (2) dephasing of the transition dipoles due to the inhomogeneous Doppler broadening. During the steady-state preparation, the homogeneous linewidth, which can be dominated by power broadening, is burned into the Doppler profile. This determines the molecular velocity bandwidth and thus the importance of dephasing in the decay rate. During the decay, power broadening will obviously be absent and cannot contribute to (1) whereas molecular collisions will. These ideas are contained in a solution of the coupled Maxwell-Schrödinger equations which yield a decay of the form $\exp(-t/T) \times \exp\{-[(\mu_{ij}\epsilon/\hbar)^2 + 1/T^2]^{1/2}t\}$, where T is the homogeneous relaxation time and $\mu_{ij}\epsilon/\hbar$ is the saturation parameter.⁴ In contrast, photon echoes are described by a decay envelope of $\exp(-t/T)$ which is independent of inhomogeneous broadening. We will report³ subsequently, in more detail, that these expectations are verified quantitatively in experiments with NH_2D where the free-induction