Light Scattering Spectroscopy: A New Method for Precise Determination of Atomic Matrix Elements

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A new approach to precise determination of atomic matrix elements is described whereby measurement of spectral locations of zeros in the Rayleigh scattering cross-section allows frequency-domain extraction of matrix elements in terms of a fiducial quantity. Illustrations are made for scattering off the ground state in Li and Cs.

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I. INTRODUCTION

An outstanding problem in experimental spectroscopy is precise determination of matrix elements describing interaction of electromagnetic radiation with matter [1]. In atomic physics, such matrix elements are important to a wide range of fundamental problems, ranging from analysis of parity violation measurements in atoms [2] to determination of the astrophysical atomic abundances [3]. In studies on atomic or molecular systems, measurement observables which determine the magnitude of matrix elements have only recently attained a relative precision of about \( \sim 10^{-3} \) in the best cases [4–9]. In contrast, other quantities such as energy level separations (\( \sim 10^{-12} \)) [10] and atomic masses (\( \sim 10^{-11} \)) [11] may be measured to an extraordinary, and much greater, relative precision. Improvements in measurement techniques, coupled with increasing sophistication of theoretical calculations, have produced a fruitful theory-experiment synergy leading to significant advances in the field.

In this paper a new method to determine atomic and molecular transition dipole matrix elements is described. Generally, this method relies on two-photon light scattering processes, such as Rayleigh or Raman scattering [1, 12]. The amplitude for these nonresonant processes depends on the contributions of the spectral distribution of intermediate states, of which often only a subset is practically important. Interference of the contributions as a function of the spectral location of so-called virtual levels for the process produces a set of zeros in the amplitude. For a given selected initial and final level, the locations of the zeros, and the associated intermediate one-photon resonances, determine the weak-field response of the atomic system. With the method, the transition matrix elements connecting the various nondegenerate states of the system may, in principle, be determined to the same level of precision as a fiducial value. The fiducial value may be derived, for example, from the measured strength of a principal resonance transition. By experimental location of related zeros in the Raman scattering or in the two-photon absorption spectrum, the relative phases of the matrix elements may also be found. The method thus achieves a mapping of matrix elements into the frequency domain, where their values may be precisely determined. It is important to note that these considerations apply generally to atomic, molecular, or solid state systems having a discrete energy spectrum.

Other authors [13] have noted in special cases the existence of zeros in the two-photon excitation spectrum. For example, Quattropani, et al. [13] have calculated in atomic H the location of zeros for several s-p-s two-photon, two-color transitions, and argued that they are a general feature of that spectrum. Experimental observation of zeros in the Rayleigh scattering spectrum due to fine- and hyperfine structure interferences have also been made in Na [14–16]. Measurements of complete destructive interference in polarization-dependent, two-photon excitation have also been made on the 3s-3p-5s [9] and 3s-3p-4d [13] transitions in Na, and on the 5s-5p-8s transition in Rb [17]. Rayleigh scattering cross-sections in the vicinity of the first resonance transition in Cs, including the location of the zero, have been calculated by Penny [13].

In the remainder of this report, the method is presented in detail for the case of Rayleigh scattering off an atomic ground level. Results are presented for the zero locations, including the contributions of energetically remote levels. Numerical illustrations are made for the cases of Li and Cs, for which precise fiducial values are available [5, 7]. Finally, it is shown how the same approach may be used to find excited-state matrix elements, in terms of the same fiducial value.

II. ANALYSIS

The fundamental expression for the Rayleigh scattering differential cross-section is well-known [1, 12], and is given, for scattering off the ground state, by

\[
\frac{d\sigma}{d\omega} = \frac{q^4 \omega^3}{16\pi^2 c^2 \hbar^2} |A|^2 \tag{1}
\]

where the scattering amplitude is
here, $\omega$ and $e$ represent the frequency and polarization of the incident radiation, while $\omega'$ and $e'$ describe the scattered radiation. The electric dipole operator is $qr$, where $q$ is the electron charge and $r$ the electron position. For elastic scattering, take $\omega = \omega'$, thereby ignoring Doppler and recoil shifts. Intermediate states are labeled as $|i\rangle$, with energy $\hbar\omega_i$, while the initial and final states are given as $|f\rangle$. The sum over intermediate states implicitly includes integration over the continuum. This contribution is normally quite small, except for the case of $H$, and will be ignored here [18]. In Eq. (2) the resonance transition, which contributes all but about 0.4 % for other transitions is typically 10 % smaller than this. Thus the location of the zeros in the Rayleigh scattering are spectrally close to the resonances (poles). Second, recent experimental advances have permitted measurement of $f$ for the first resonance transitions to a precision of about $10^{-3}$ in some cases. This is to be compared to a typical precision of 10 % for transitions to more energetic levels. While other excited levels do contribute to the process, the contribution is small, and needs only be approximately known. The spectral separation between an atomic resonance at $\omega_i$ and the associated zero at $\omega_i + 1$ is determined mainly by the matrix elements coupling the ground level to level $i$, relative to the matrix elements associated with the resonance transition.

III. ILLUSTRATIONS

The above considerations are illustrated by means of a particular geometry and applied to Rayleigh scattering off the $^2S_{1/2}$ ground level of Cs and Li. Consider the situation shown in Fig. 1, where the exciting radiation is taken to propagate along the y-axis, and is linearly polarized along either the z-axis or x-axis. The scattered radiation is detected through a linear polarization analyzer oriented so as to transmit the component of the scattered radiation polarized along the z-axis. Evaluation of Eq. (2) for frequencies in the neighborhood of a multiplet $np$ gives

\[
A = \sum_i \frac{\langle f | e \cdot r | i \rangle \langle i | e' \cdot r | f \rangle}{\omega_i + \omega'} + \frac{\langle f | e' \cdot r | i \rangle \langle i | e \cdot r | f \rangle}{\omega_i - \omega}
\]

for transitions out of the ground level of many atoms. To see this, note first that the transition strength for excitation out of the ground level is normally concentrated in the lowest-energy-allowed transition [19, 22]. For example, in the alkali- and alkaline earth-metal atoms, the oscillator strength [23] of the first resonance transition is about $f = 1$, while $f_i$ for other transitions is typically 10 times smaller than this. Thus the location of the zeros in the Rayleigh scattering are spectrally close to the resonances (poles).
\[ A_{zz}^n = \frac{1}{9} \left( \frac{2M_{n3/2}}{\Delta_n} + \frac{M_{n1/2}}{\Delta_n + \Delta_{fs}^n} \right) + \frac{2M_{n3/2}}{\Delta_n - 2\omega} + \frac{M_{n1/2}}{\Delta_n + \Delta_{fs}^n - 2\omega} - P_{zz}^n \]  

(3)

\[ A_{xz}^n = -\frac{1}{9} \left( \frac{M_{n3/2}}{\Delta_n} - \frac{M_{n1/2}}{\Delta_n + \Delta_{fs}^n} \right) - \frac{M_{n3/2}}{\Delta_n - 2\omega} + \frac{M_{n1/2}}{\Delta_n + \Delta_{fs}^n - 2\omega} - Q_{zz}^n \]  

(4)

In these expressions, \( M_{nj} \) represents the squared radial transition matrix elements connecting the ground level with a particular level \( nj \), where \( n \) is the principal quantum number and \( j \) the angular momentum quantum number. They are defined as

\[ M_{nj} = \left| \int_0^\infty R_{nlj}(r)R_{nl'lj'}(r)r^3 dr \right|^2. \]  

(5)

where \( l = 1, \) and \( l = 0 \), are the orbital angular momenta of the excited and ground levels. In the definition, the \( j \)-dependence due to angular momentum recoupling has been included in Eq. 3 - 4, leaving only intrinsic \( j \)-dependence due to relativistic mixing of the spin-orbit levels. The detuning \( \Delta_n = \omega - \omega_{n3/2} \), is the offset of the radiation from resonance with the \( n \) \( 2P_{3/2} \) level, while \( \Delta_{fs}^n \) is the fine-structure splitting in the multiplet \( n \). The quantities \( P_{nzz} \) and \( Q_{nzz} \) represent the contributions, from all other levels, to the Rayleigh scattering amplitude:

\[ P_{zz}^n = \sum_{i\neq n} \left( \frac{2M_{i3/2}}{\omega_{i3/2} - \omega} + \frac{M_{i1/2}}{\omega_{i1/2} - \omega} \right) \]  

\[ + \frac{2M_{i3/2}}{\omega_{i3/2} + \omega} + \frac{M_{i1/2}}{\omega_{i1/2} + \omega} \]  

(6)

\[ Q_{zz}^n = \sum_{i\neq n} \left( \frac{M_{ni3/2}}{\omega_{i3/2} - \omega} - \frac{M_{ni1/2}}{\omega_{i1/2} - \omega} \right) \]  

\[ - \frac{M_{i3/2}}{\omega_{i3/2} + \omega} + \frac{M_{i1/2}}{\omega_{i1/2} + \omega} \]  

(7)

As in Eq. 1, these amplitudes permit definition of a linear depolarization degree in terms of intensities \( \sigma_{zz} \) and \( \sigma_{xz} \):

\[ P_L = \frac{\sigma_{zz} - \sigma_{xz}}{\sigma_{zz} + \sigma_{xz}} \]  

(8)

A. Application to Cs Rayleigh Scattering

Using experimental data for Cs \[22\], \( P_L \) has been calculated as a function of \( \Delta_7 \) for Rayleigh scattering in the vicinity of the \( 6s^2S_{1/2} \to 7p^2P_j \) second resonance transitions. Knowledge of matrix elements for these transitions is important for analysis of parity violation experiments in atomic Cs, and the present scheme is directly applicable to that case. The results are presented in Fig. (2), and show the existence of two critical frequencies where \( A_{zz} = 0 \) and \( P_L = -100 \% \). For the data of \[22\], these are located at about -43.25 cm\(^{-1}\) and at -195.2 cm\(^{-1}\), relative to resonant scattering from the \( 7p^2P_{3/2} \) level. Roughly speaking, the zero between the resonance transitions arises from interference between the scattering from the two \( 7p \) fine-structure components, while that to the low-energy side of the \( 6s^2S_{1/2} \to 6p^2P_j \) resonance transition, and so the location of the lower frequency zero is determined primarily by the very well-known \((< 10^{-3}) \) 6p matrix elements, and the \( 7p \) matrix elements. The much less-well-known \( 6s^2S_{1/2} \to np^2P_j \) matrix elements \( (n \leq 7) \) contribute only weakly to the null location, and their contribution needs only to be estimated. Thus, precise experimental determination of the \( P_L = -100 \% \) points directly allows extraction of the unknown quantities; the dipole matrix elements for the \( 6s^2S_{1/2} \to 7p^2P_j \) transitions. Previous polarization measurements \[17\] in two-photon, two-color excitation in Rb have shown that precise determination of the spectral location \( (\sim \pm 10^{-2} \text{cm}^{-1}) \) of the zeros is possible. In addition, the Rayleigh scattering cross-section for these transitions is large, and the relative scattering intensity may be readily measured. For this case, the matrix elements may be determined to \(< 10^{-3} \), limited primarily by the precision of the fiducial resonance line oscillator strengths.

B. Application to Li Rayleigh Scattering

\[ \begin{array}{cccc}
 n & \omega_{oi} - \omega_i (\text{cm}^{-1}) & \text{Numerical} & \text{Numerical (2p only)} \ \text{Approx.} & \text{Analytical} \\
 \hline
 3 & -38.37 & -38.07 & -38.44 \\
 4 & -33.10 & -32.96 & -33.17 \\
 5 & -25.24 & -25.43 & -25.29 \\
 6 & -16.70 & -17.15 & -16.72 \\
\end{array} \]

The Li atom is also an interesting case, for it has the complexity of a three-electron system, and yet should be
FIG. 2: Calculated linear polarization spectrum for Rayleigh scattering in the vicinity of the 6s $^3S_{1/2} \rightarrow 7p^2P_{j/2}$ (j = 1/2, 3/2) second resonance transitions, illustrating the location of the two zeros in $A_{zz}$ where $P_L = -1.0$.

A new method for determining transition matrix elements has been described. The technique relies on measurement of Rayleigh scattering off ground and excited levels of atoms. Location of zeros in the scattering cross-section, or measurement of the polarization dependence of the scattered intensity, permits determination of the matrix elements in terms of a well-known fiducial quantity, which can be the matrix elements of the principal resonance transition. The approach is appealing because it can lead to high relative precision ($< 10^{-3}$) in the matrix elements, and because it is a frequency domain method which describes spectroscopy of energy level locations and of matrix elements in a uniform manner.

C. Application to determination of excited-level matrix elements

Once transition matrix elements for the gs - np principal series are determined, it is possible to extend the scheme through a stepwise process in which a gs - np transition is resonantly excited with one light source. Measurements of Rayleigh scattering off excited np levels are then made with a second light source. There are zeros in the np - n's and np - n'd scattering amplitudes, resulting in determination of relative transition matrix elements as before. The np - n's and np - n'd contributions may be distinguished through their different dependence on light polarization, even in the absence of spin-orbit interaction. The relative measurements may be put on an absolute scale through the previously determined gs - np matrix elements, for the np - gs transition also contributes to the excited-level Rayleigh scattering. This approach may evidently be extended to scattering off other excited levels, and matrix elements similarly determined.

IV. CONCLUSIONS

A new method for determining transition matrix elements has been described. The technique relies on measurement of Rayleigh scattering off ground and excited levels of atoms. Location of zeros in the scattering cross-section, or measurement of the polarization dependence of the scattered intensity, permits determination of the matrix elements in terms of a well-known fiducial quantity, which can be the matrix elements of the principal resonance transition. The approach is appealing because it can lead to high relative precision ($< 10^{-3}$) in the matrix elements, and because it is a frequency domain method which describes spectroscopy of energy level locations and of matrix elements in a uniform manner.
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[1] Claude Cohen-Tannoudji, Jacques Dupont-Rec, and Gilbert Grynberg, Atom-Photon Interactions: Basic Processes and Applications, (John Wiley and Sons, Inc., New York, 1992); Rodney Loudon, Quantum Theory of Light, 2nd Ed. (Oxford University Press, 1983).
[2] M.C. Noecker, B.P. Masterson, and C.E. Wieman, Phys. Rev. Lett. 61, 310 (1988); M.A. Bouchiat, Atomic Physics 12, AIP Conference Proceedings 232, ed. J.C. Zorn and R.R. Lewis, AIP (New York, 1990).
[3] D. Mihalas, Stellar Atmospheres, (Freeman, San Francisco, 1970).
[4] Dirk Goebel and Uwe Hohm, Phys. Rev. A52, 3691 (1995); M.A. Kadar-Kallen and K.D. Bonin, Phys. Rev. Lett. 72, 828 (1994).
[5] C.R. Ekstrom, J. Schmiedmayer, M.S. Chapman, T.D. Hammond, and D.E. Pritchard, Phys. Rev. A51, 3883 (1995); W.I. McAlexander, E.R.I. Abraham, N.W.M. Ritchie, C.J. Williams, H.T.C. Stoof, and R.G. Hulet, Phys. Rev. A51, R871 (1995); H. Wang, J. Li, X.T. Wang, C.J. Williams, P.L. Gould, and W.C. Stwalley, Phys. Rev. A55, R1569 (1997).
[6] C.W. Oates, K.R. Vogel, and J.L. Hall, Phys. Rev. Lett. 76, 2866 (1996).
[7] R.J. Rafec, C.E. Tanner, A.E. Livingston, K.W. Kukla, J.G. Berry, and C.A. Kurtz, Phys. Rev. A 50, R1976 (1994); L. Young, W.T. Hill III, S.J. Sibener, S.D. Price, C.E. Tanner, C.E. Wieman, and S.R. Leone, Phys. Rev. A55, R1569 (1997).
[8] U. Volz, M.Jajerus, H. Liebel, A. Schmitt, and H. Schmoranzer, Phys. Rev. Lett. 76, 2862 (1996). U. Volz and H. Schmoranzer, Physica Scripta T65, 48 (1996).
[9] R.P. Meyer, A.I. Beger, and M.D. Havey, Phys. Rev. A55, 230 (1997).
[10] P. Shao, W. Lichten, H. Layes, J. Bergquist, Phys. Rev. Lett. 58, 1293 (1987); T. W. Husch, "Precision Spectroscopy of Atomic Hydrogen," in Atomic Physics 14, ed. Wineland, C.E. Wieman, and S.J. Smith, AIP Conference Proceedings (New York, 1995).
[11] F. DiFillipo, V. Natrajian, K.R. Boyce, and D.E. Pritchard, Phys. Rev. Lett. 73 1481 (1994).
[12] Dietrich Marcuse, Principles of Quantum Electronics, (Academic Press, New York, 1980).
[13] A. Quattropani, F. Bassani and Sandra Carillo, Phys. Rev. A25, 3079 (1982); J.H. Tung, A.Z. Tang, G.J. Salamo, and F.T. Chan, J. Opt. Soc. Am. B3, 837 (1986); J.H. Tung, X.M. Ye, G.J. Salamo, and F.T. Chan, Phys. Rev. A30, 1175 (1984); C.M. Penney, J. Opt. Soc. Am. 59, 34 (1969); J.E. Bjorkholm and P.F. Liao, Phys. Rev. Lett. 33, 128 (1974).
[14] A.C. Tan and C.K. Au, Optics Comm. 19, 265 (1976).
[15] R. Walkup, A.L. Migdall, and D.E. Pritchard, Phys. Rev. A25, 3114 (1982).
[16] D. Zei, R.N. Compton, J. Stockdale, M. Pindzola, Phys. Rev. A40, 5044 (1989).
[17] A. I. Beger, M.D. Havey, and R.P. Meyer, Phys. Rev. A 55, 3780 (1997).
[18] H.A Bethe and E.E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms, (Springer-Verlag, Berlin, 1957).
[19] W.L. Weise, M.W. Smith, B.M. Miles, Atomic Transition Probabilities: Sodium Through Calcium, Natl. Bur. Stand. (U.S. GPO, Washington, D.C. 1966, 1969), V. 1-2; A. Lindgd and S.E. Hielson, Atomic Data and Nuclear Data Tables, v.19 (Academic Press, 1977); D.R. Bates and A. Damgaard, Phil. Tran. Roy. Soc. Lon. 242, 101 (1949).
[20] C.E. Theodosiou, J.J. Curtis, C.A. Nicolaides, Phys. Rev. A 52, 3677 (1995).
[21] D.R. Beck, C.A. Nicolaides, Chem. Phys. Lett. 49, 357 (1977).
[22] A.A. Radzig and B.M. Smirnov, Reference Data on Atoms, Molecules, and Ions (Springer-Verlag, Berlin, 1985).
[23] The oscillator strength is related to the squared matrix elements by

\[ f_{ik} = \frac{2m\omega_{ik}}{i|\langle q|\hat{r}\rangle_{k}^{2}|^{2}/\hbar(2J_i + 1), \]

where q and m are the electron mass and charge, and \( J_i \) the angular momentum of the level i.
[24] For a ground multiplet split by the spin-orbit interaction, detection of Raman scattered light, rather than the Rayleigh scattered radiation, can greatly improve the signal-to-background ratio.