

Nonrelativistic High-Energy Photoionization Cross Section*

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It is shown that the use of the dipole acceleration form of the photoionization cross section in a high-energy Born expansion gains one iteration of the Born series over the corresponding expansion of the dipole-velocity cross section. Some comparisons with Hartree-Fock indicate the domain of validity of the acceleration Born approximation.

I. INTRODUCTION

IN the calculation of the atomic contribution to opacities one is concerned with the evaluation of the atomic photoionization cross section for large numbers of atomic states. Thus, reliable approximation methods are necessary.

For photon energies not too much greater than the photoionization threshold, the phase-shifted Coulomb approximation of Burgess and Seaton¹ seems to provide reliable estimates. The energy range of validity of this approximation requires that the momentum of the ejected electron (in atomic units) be much less than the charge of the residual ion.

For photon energies much greater than threshold, however, where one might expect the validity of the Born approximation to the free-electron wave function, the results are misleading. Indeed, as shown in Bethe and Salpeter,² the first Born approximation to the dipole-velocity matrix element in hydrogen gives an incorrect high-energy limit, and the correct high-energy form is obtained only through inclusion of the second Born approximation. Similar behavior has been noted by Salpeter³ and by Dalgarno and Stewart.⁴

The purpose of this paper is to show that the use of the dipole-acceleration form of the photoionization matrix element avoids this difficulty and leads to the correct high-energy limit in first Born approximation.

II. THE DIPOLE ACCELERATION MATRIX ELEMENT

We are concerned with electron energies far above the photoionization threshold—specifically, such that the electron momentum is much greater than the charge of the residual ion—but below energies at which relativistic considerations enter. For such energies a one-electron approximation with neglect of exchange is probably valid, and the electric dipole matrix ele-

ment \mathbf{D} takes the form

$$\mathbf{D} = \langle f | \mathbf{p} | i \rangle \approx \left(\phi_k + \frac{1}{\epsilon_k - i\eta - H_0} V \psi_b | \mathbf{p} | \psi_b \right), \quad (1)$$

where $|i\rangle$ is approximated by the one-electron wave function of the initial bound state—assumed known—and $|f\rangle$ is the final-state free-electron wave function ψ_k written in terms of the Lippman-Schwinger equation. Here k labels the electron momentum, V is the interaction of the electron with the rest of the system, and both ψ_k and ψ_b are eigenstates of the total one-electron Hamiltonian ($H_0 + V$) with eigenvalues ϵ_k and ϵ_0 , respectively. ϕ_k is the asymptotic free-electron state—a plane wave—and is an eigenstate of the kinetic energy H_0 with eigenvalue ϵ_k . \mathbf{p} is the electron momentum operator.

The Born series of approximations consists of iterating the Lippman-Schwinger equation for the free-electron wave function, and is usually considered to be an expansion in powers of the ratio of some average electron interaction B to the excitation energy ($\epsilon_k - \epsilon_0$), which is the photon energy ω_k . However, the presence of the electron momentum \mathbf{p} in the matrix element destroys this convergence behavior.

The first Born approximation is given by ϕ_k alone, and the second Born approximation is given by

$$\mathbf{D}^{(2)} = \left(\phi_k \left| V \frac{1}{\epsilon_k + i\eta - H_0} \mathbf{p} \right| \psi_b \right). \quad (2)$$

Commuting \mathbf{p} with H_0 , replacing H_0 by the total Hamiltonian H , and allowing H to operate on ψ_b gives

$$\begin{aligned} \mathbf{D}^{(2)} &= (\phi_k | V \mathbf{p} | \psi_b) (1/\omega_k) + o(B/\omega_k) \\ &= (\phi_k | \mathbf{p} V - [\mathbf{p}, V] | \psi_b) (1/\omega_k) + o(B/\omega_k), \end{aligned} \quad (3)$$

where the correction term of order (B/ω_k) comes from the replacement of H_0 by H . Then V on ψ_b gives $(\epsilon_0 - H_0)$, commuting with \mathbf{p} and giving $(-\omega_k)$ when operating on ϕ_k . Thus, the result is obtained

$$\mathbf{D}^{(2)} = -\mathbf{D}^{(1)} - (\phi_k | [\mathbf{p}, V] / \omega_k | \psi_b) + o(B/\omega_k). \quad (4)$$

The first term is the negative of the first Born approximation to the dipole velocity matrix element and the second term is seen to be the first Born approximation to the dipole-acceleration matrix element.

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¹ A. Burgess and M. J. Seaton, *Monthly Notice Roy. Astron. Soc.* **120**, 121 (1960).

² H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 70.

³ P. Kabir and E. Salpeter, *Phys. Rev.* **108**, 1256 (1957).

⁴ A. Dalgarno and A. Stewart, *Proc. Phys. Soc. (London)* **76**, 49 (1960).

Therefore, the sum of the first two Born approximations to the velocity matrix element is equivalent to the first Born approximation to the acceleration matrix element—with neglect of terms of order (B/ω_k) .

An evaluation of the third Born approximation to the velocity matrix element has been carried through—one must go back and pick up an extra term from the expansion of the propagator [Eqs. (2) to (3), above] in order to keep all terms of order (B/ω_k) . A similar result is obtained: The sum of the first three velocity Born approximations is equivalent to the sum of the first two terms of the acceleration Born series, with neglect of terms of order $(B/\omega_k)^2$.

Thus the use of the acceleration form of the dipole matrix element in a Born expansion gains one iterate over the corresponding Born series for the dipole-velocity matrix element. The resulting series is indeed an expansion in increasing powers of (B/ω_k) . A calculation of the first Born approximation to the dipole-acceleration photoionization cross section in hydrogen—analogue to the calculation in Bethe and Salpeter²—leads to the correct high-energy behavior.

III. COMPARISON WITH HARTREE-FOCK CALCULATIONS

The photoionization cross section of ground-state helium has been evaluated in the dipole acceleration first Born approximation. The results are shown in Fig. 1. The bound-state wave function is the six-parameter Hylleraas function utilized by Stewart and Webb⁵ in their Hartree-Fock calculation, which results are included in the figure. Also included are the low-energy cross section obtained from the approximation of Burgess and Seaton¹ and some recent experimental results of Lowry and Tomboulia.⁶

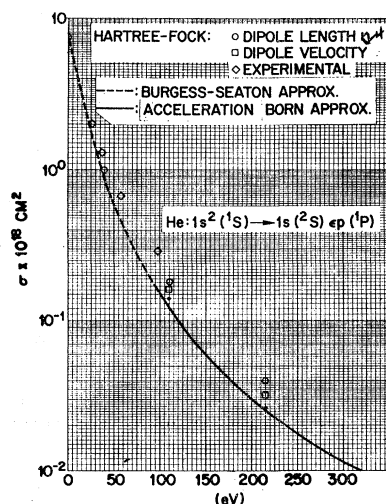


FIG. 1. The photoionization cross section of ground-state helium versus electron energy. The two dark dots (at 110 and 215 eV) are the results of a Hartree-Fock calculation of the dipole-acceleration cross section by Stewart and Webb (Ref. 5).

⁵ A. Stewart and T. Webb, Proc. Phys. Soc. (London) 82, 532 (1963).

⁶ J. F. Lowry and D. H. Tomboulia, Bull. Am. Phys. Soc. 9, 51 (1964).

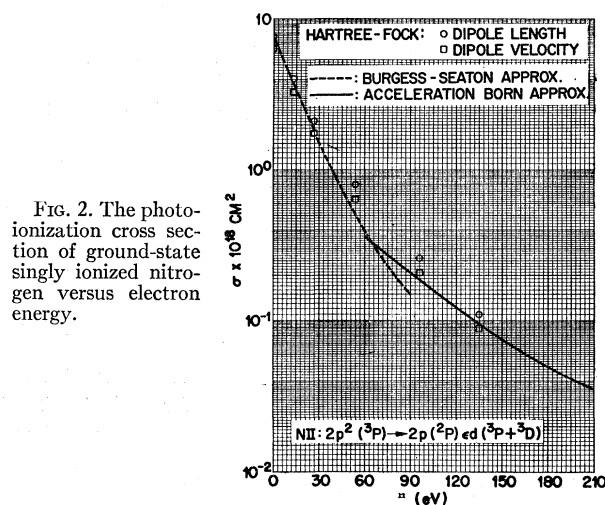


FIG. 2. The photoionization cross section of ground-state singly ionized nitrogen versus electron energy.

The corresponding results for the ground-state photoionization of nitrogen II are presented in Fig. 2. The bound-state wave function is a self-consistent field (SCF) function of Roothaan and Kelly,⁷ and the Hartree-Fock results were obtained using a code by Dalgarno, Henry, and Stewart and kindly provided to us by Professor Dalgarno.

The plane-wave Born approximation is a good approximation to a more correct Coulomb matrix element in the approximation that the electron momentum k be much greater than the residual charge Z on the ion—the complement of the validity condition for the Burgess-Seaton approximation. In the case of NII, $k=Z$ at approximately 55 eV, and each approximation seems quite good within its domain of validity.

IV. CONCLUSIONS

The results presented in this paper concern the convergence of the Born series for the continuum electron wave function when utilized in a photoionization calculation and assumes exact bound-state wave functions. The use of variationally determined wave functions for the bound state leads to questions concerning the reliability of such functions at various radii.⁸ Such questions are not considered here. Further, this one-electron treatment does not admit of resonance and other many-body effects.

The greater accuracy of the acceleration matrix element at high energies is in agreement with the familiar argument that high energies preferentially sample short distances and low energies, long distances. The acceleration matrix element gives greater weight to the short-range parts of the wave function than does the

⁷ C. Roothaan and P. Kelly, Phys. Rev. 131, 1177 (1963).

⁸ S. Chandrasekhar, Rev. Mod. Phys. 16, 301 (1944).

momentum matrix element. Similarly, the Burgess-Seaton approximation—which is a dipole length approximation—gives greater weight to the long-range parts of the wave function and is specifically a low-energy approximation.

Results such as those shown lead us to the expectation that a use of the dipole acceleration Born approximation with the Burgess-Seaton approximation results in a representation of the atomic photoionization cross section of accuracy suitable for most opacity calculations.

Rotational Magnetic Moments*

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The presence in molecular-beam magnetic resonance of transitions with $\Delta m \gg 1$ has made possible measurements of gyromagnetic ratios which are very much smaller than the nuclear magneton. Such low values are normally associated with the rotation of Σ molecules. The following values of g_J in nuclear magnetons per rotational quantum number have been determined in this way: CO_2 , (-0.05508 ± 0.00005) ; OCS , -0.02889 ± 0.00002 ; CS_2 , (-0.02274 ± 0.00002) ; C_2H_2 , -0.04903 ± 0.00004 ; $\text{Fe}(\text{CO})_5$, 0.0210 ± 0.0005 ; $\text{Ni}(\text{CO})_4$, 0.0179 ± 0.0005 ; CF_4 , 0.031 ± 0.005 . The sign of g_J in C_2H_2 has been found to be the same as that in OCS , which was known to be negative. The signs in parentheses are assumed. The technique also gives the spin-rotational interaction constant in C_2H_2 as 3.58 ± 0.01 kc/sec.

I. INTRODUCTION

IT has been shown previously¹ that transitions of $\Delta m_J \gg 1$ in molecular beam magnetic resonance of rotational moments give rise to deflections which are much greater than would otherwise be possible for the very small gyromagnetic ratios. Because of this it has been possible to make direct measurements of several rotational moments. Certain gaseous molecules which have been studied using the apparatus with an electron bombardment detector are reported in this paper.

II. OSCILLATING FIELD REQUIREMENTS

The main modification of the apparatus from the original nuclear moment design involved the transition-producing oscillating field. The optimal magnitude of the rotating component is given by¹

$$H_1 = 1.2H_0\alpha/\omega_0l.$$

Using a flattened solenoid coaxial with the beam to produce the field, the current required becomes

$$I = (11.4/gN)(T/M)^{1/2},$$

where I is the current in amperes, g the gyromagnetic ratio in nuclear magnetons per rotational quantum number, N the total number of turns in the solenoid, T the source temperature in degrees Kelvin, and M the molecular weight. For the molecule OCS at room

temperature, $NI \approx 900$ At is required. The frequency in a field of 5000 G (the maximum for our C magnet) would be about 110 kc/sec.

In order to obtain the maximum number of turns, coils were made to fill the entire 20-in. C -magnet length except for the space occupied by the collimator in the middle. These coils had 64 turns each, so that the optimal current for OCS was about 7 A. The source of power for the coils was a McIntosh 60-W hi-fi amplifier which would supply about 4 A at 60 kc/sec. Because of the drop in field near the ends of the magnet, however, it was not possible to use the full length at the full field. The best value of the OCS moment was obtained using only 22 turns on each side in a field of about 900 G. All of the results reported here were observed using less than the optimal current. The technique used the two separated coils in series with phase reversal modulation of the second. This gives an interference pattern like that shown for OCS in Fig. 1.

III. EXPERIMENTAL RESULTS

All of the molecules studied, excepting C_2H_2 and CF_4 , contain only spinless nuclei, so the spectrum of each consisted of a single pure line at the Larmor frequency of the rotational moment. In C_2H_2 there is a splitting into three lines caused by the spin-rotational interaction, as shown in the recorder trace of Fig. 1. The central line, with $m_I = 0$, has contributions from all the para- C_2H_2 molecules and from one third of the ortho- C_2H_2 molecules for a total of one half the total intensity. The side peaks, each of one quarter the total intensity, are separated from the central line by just the spin-rotational interaction constant c , which can

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¹ J. W. Cederberg and N. F. Ramsey, Phys. Rev. 135, A39 (1964).