Sum Rules for Neon Photoeffect*

K. R. PIECH† AND J. S. LEVINGER‡
Cornell University, Ithaca, New York
(Received 14 February 1964)

Three oscillator sum rules are evaluated for neon from available experimental cross-section data. Recent data of Ederer and Tomboulian are used for the region from threshold to 13 Ry, and standard power-law expressions are fitted for the region from 13 Ry to the K edge. Beyond the K edge the Stobbe law and Born approximation are utilized. An independent value for the polarizability is utilized to determine the discrete contribution to the polarizability sum rule. This discrete contribution is used to determine the discrete contributions to the remaining sum rules. Hartree-Fock wave functions are used in evaluation of terms such as $\langle 0|\sum_{i\neq j}\mathbf{r}_i\cdot\mathbf{r}_j|0\rangle$ and $\langle 0|\sum_{i\neq j}\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle$. (1) The diamagnetic susceptibility by sum rule is $(-7.05\pm0.50)\times10^{-6}$ versus a directly measured value of $(-7.65\pm0.1)\times10^{-6}$. (2) The neon binding energy by sum rule of 276 ± 13 Ry contrasts with 257.88 ± 0.01 Ry otherwise. (3) The sum rule using the squared energy yields $(11.2\pm0.6)\times10^4$ Ry^2 versus $(10.4\pm1.0)\times10^4$ Ry^2 by Hartree-Fock calculation of the electron density at the nucleus.

I. INTRODUCTION

RECENTLY, Ederer and Tomboulian[1] have determined the absorption cross section of neon from 80 to 600 Å, and have been able to verify the Thomas-Reiche-Kuhn and polarizability sum rules for neon. Utilizing the Ederer-Tomboulian data and previous cross-section data for neon in other energy ranges, it is possible to extend oscillator sum calculations for neon to all of the standard nonrelativistic sum rules.

If energies are expressed in rydbergs, and all other quantities in atomic units, the oscillator strength f_{n0} is defined as

$$f_{n0}=(W/3)|\langle n|\sum_i \mathbf{r}_i|0\rangle|^2. \quad (1)$$

Here $\mathbf{r}_i$ is the position of the ith electron, E_0 and E_n being the binding energies of the ground and nth excited states, $W=E_n-E_0$, and the summation runs over all electrons of the atom.

The oscillator sum rules μ_p in these units are[2]

$$\mu_{-2}=\sum_n f_{n0}W^{-2}=\alpha/4, \quad (2)$$

$$\mu_{-1}=\sum_n f_{n0}W^{-1}=\langle 0|(\sum_i \mathbf{r}_i)^2|0\rangle/3, \quad (3)$$

$$\mu_0=\sum_n f_{n0}=Z, \quad (4)$$

$$\mu_1=\sum_n f_{n0}W=\tfrac{4}{3}\{E_0+\tfrac{1}{2}\sum_{i\neq j}\langle 0|\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle\}, \quad (5)$$

$$\mu_2=\sum_n f_{n0}W^2=(16\pi Z/3)\sum_i \langle 0|\delta(\mathbf{r}_i)|0\rangle. \quad (6)$$

Here α is the polarizability; $\mathbf{p}_i$ is the momentum of the ith electron, and Z is the atomic number. The sum is over all excited states n of the atom.

Equation (2) may readily be proved by a first-order perturbation applied to an atom in an electric field.[3] μ_{-1} may be related to the diamagnetic susceptibility χ since $\chi\sim\langle 0|\sum_i r_i^2|0\rangle$, by means of the formula[4] (for a mole)

$$\chi=-7.92\times10^{-7}[3\mu_{-1}-\sum_{j\neq k}\langle 0|\mathbf{r}_j\cdot\mathbf{r}_k|0\rangle]. \quad (7)$$

μ_0 is the well-known Thomas-Reiche-Kuhn rule.

For μ_1 we express $\langle 0|(\sum_i \mathbf{p}_i)^2|0\rangle$ as $\langle 0|\sum_i p_i^2|0\rangle+\langle 0|\sum_{i\neq j}\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle$. From the virial theorem, the first term is twice the binding energy.

μ_2 may be determined by noting that[5]

$$\sum_n f_{n0}W^2=\tfrac{4}{3}\sum_{i,j}(\nabla_i\cdot\nabla_j V)_{00} \quad (8)$$

and setting $V=-\sum_k Z/r_k+\sum_{k<l}1/|\mathbf{r}_k-\mathbf{r}_l|$. A standard calculation yields Eq. (6): The first term gives the $\delta(\mathbf{r}_i)$, and the second term gives zero.

II. EXPERIMENTAL DATA

For calculations of $\mu_p=\sum_n f_{n0}W^p$ we need knowledge of the oscillator strength for discrete transitions and the oscillator density for the continuum. At present there are no neon measurements available for the cross section due to discrete transitions. The oscillator density is proportional to the cross section for photoionization.

The data of Ederer and Tomboulian[6] in the region 1.6–13 Ry are available in this region, and the experimental cross section curves were numerically integrated to determine the contribution from this region (Table I). For 13 to 228 Ry, measurements of the cross section are available.[7] In this region the cross section may be repre-

* Supported in part by the Office of Naval Research.
† National Science Foundation Fellow.
‡ AVCO Visiting Professor.
[1] D. L. Ederer and D. H. Tomboulian, Phys. Rev. **133**, A1525 (1964).
[2] A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A70**, 802 (1957).
[3] N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Clarendon Press, Oxford, 1950), p. 168.
[4] J. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 91.
[5] J. S. Levinger, *Nuclear Photo Disintegration* (Oxford University Press, London, 1960).
[6] D. L. Ederer, Ph.D. thesis, Cornell University, 1963 (unpublished).
[7] E. Dershem and M. Schein, Phys. Rev. **37**, 1238 (1931); and A. J. Bearden, Bull. Am. Phys. Soc. **8**, 312 (1963).

TABLE I. Contributions to oscillator sum rules, neon (a.u.).

Region (Ry)	Form	μ_{-2} $(\text{Ry})^{-2}$	μ_{-1} $(\text{Ry})^{-1}$	μ_0	μ_1 Ry	μ_2 $(\text{Ry})^2$
Discrete	Mean energy determination	0.13	0.19	0.26	0.4	···
1.6–13.0	Average of two experimental curves (Ederer)	0.54	1.68	6.89	37.1	300
13.0–63.7	$1.39\times10^2\ W^{-2.59}$	···	0.07	1.36	31.4	1000
63.7–227.8	$4.02\times10^3\ W^{-2.72}$	···	0.02	1.63	167.0	19 600
227.8–911.3	$1.37\times10^4\ W^{-2.89}$	···	···	0.17	64.5	26 800
911.3–7353	Stobbe formula	···	···	0.01	16.7	31 900
7353–∞	$1.37\times10^6\ W^{-3.50}$	···	···	···	1.4	32 000
	Sum	0.67	1.96	10.32	318.5	111 600

sented by a pair of power laws, the first in the region from 13 Ry to K edge, and the second from the K edge to 228 Ry. Analytic integrations give the contributions to μ_p in the region 13–228 Ry.

The behavior in the region from 228 to 911 Ry was obtained by fitting a power law to the experimental data of Allen.[8]

The region from 911 to 7353 Ry was treated using data from the Stobble formula calculated by Bearden[9] for the neon atom.

Figure 1 shows that the experimental photoeffect cross sections of Allen for 911–2200 Ry confirm the Bearden calculation. We have subtracted Compton scattering from Allen's total cross sections by means of the Klein-Nishina formula.

The $\frac{7}{2}$ power law was then assumed to hold above 7353 Ry with constants determined theoretically by the Born approximation for the $1s^2$ shell[10]:

$$\sigma=\sigma_0[Z^5/(137)^4]4\sqrt{2}(mc^2/W)^{7/2}$$
$$=1.37\times10^6 W^{-7/2}\ \text{a.u.},\quad (9)$$

where σ_0 is the Thomson cross section.

While Eq. (9) gives a cross section appreciably greater than the experimental one at lower energies, the result is accurate enough in the region we are now concerned with. Figure 1 gives the data of Bearden, Allen, and the $\frac{7}{2}$ power law in the region considered. Of course, the experimental photoeffect cross sections do not follow a $\frac{7}{2}$ power law at very high energies ($\approx 20\,000$ Ry$=mc^2$) due to relativistic effects. We have forced the data to follow a nonrelativistic $W^{-7/2}$ expression so that we can compare with the nonrelativistic sum rules (2)–(6). We do not know of rigorous relativistic analogs[11] to Eq. (4), and Eqs. (5) and (6) diverge in relativistic calculations. We are attempting to neglect relativistic effects in a consistent manner.

Table I describes the form of the contribution in each region of the continuum and its magnitude. The determination of values for discrete transitions is discussed in the next section.

III. COMPARISON WITH INDEPENDENT EXPERIMENTAL DATA

In Sec. I relations between the quantities μ_p ($p=\pm2, \pm1, 0$), the polarizability α, the diamagnetic susceptibility χ, and the atomic binding energy E_0, were given.

In work with μ_{-2}, the polarizability α was taken to be that measured by Cuthbertson and Cuthbertson,[12]

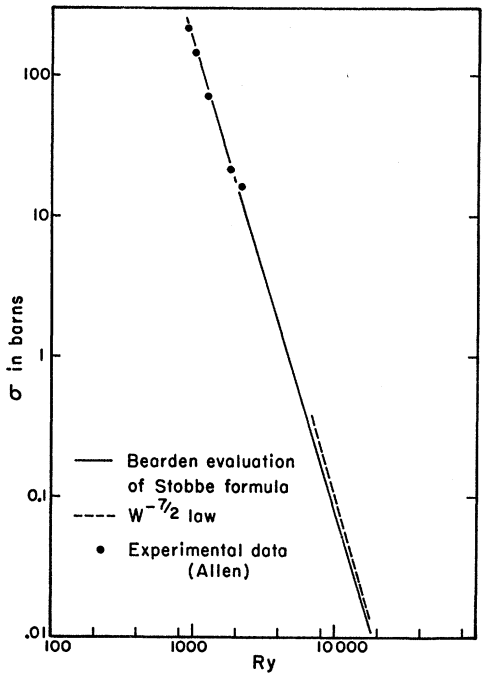

FIG. 1. Comparison of theoretical and experimental photoeffect cross sections for neon: The points are from Allen, Ref. 8; the solid line is the Stobbe formula evaluated by Bearden; the dashed line is the $W^{-7/2}$ Born-approximation result.

[8] S. J. M. Allen: see *X-rays in Theory and Experiment*, by Arthur H. Compton and Samuel K. Allison (D. Van Nostrand and Company, Inc., New York, 1935).
[9] A. J. Bearden (private communication).
[10] W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1954), p. 267.
[11] J. S. Levinger and M. L. Rustgi, Phys. Rev. **103**, 439 (1956).
[12] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A84**, 13 (1911).

TABLE II. Comparison of sum-rule results with other data.

Rule p		Sum-rule photoeffect calculation	Other experiment
-1	χ	$-(7.05\pm0.50)\times10^{-6}$	$-(7.65\pm0.1)\times10^{-6}$
0	Z	10.3 ± 0.5	10 ± 0.000
1	E_0	276 ± 13 Ry	257.88 Ry
2	μ_2	$(11.2\pm0.6)\times10^4$ Ry^2	$(10.4\pm1.0)\times10^4$ Ry^2

$\alpha=0.398\times10^{-24}$ cm^3. The diamagnetic susceptibility is given by Havens[13] as $\chi=-(7.65\pm0.1)\times10^{-6}$. The nonrelativistic binding energy E_0 is given by Scherr *et al.*[14] as $E_0=257.88$ Ry with an error of less than 0.01 Ry.

In order to relate the sum rules[15] to experimental data it is necessary to calculate $\sum_{i\neq j}\langle 0|\mathbf{r}_i\cdot\mathbf{r}_j|0\rangle$, $\sum_{i\neq j}\langle 0|\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle$ and $\langle 0|\nabla^2V|0\rangle$. The wave functions of Duncanson[16] were used in the determination of $\sum_{i\neq j}\langle 0|\mathbf{r}_i\cdot\mathbf{r}_j|0\rangle$ and $\sum_{i\neq j}\langle 0|\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle$. For $\langle 0|\nabla^2V|0\rangle$ the wave functions determined by Worsley[17] were used. The results (in a.u.) are

$$\sum_{i\neq j}\langle 0|\mathbf{r}_i\cdot\mathbf{r}_j|0\rangle=-3.01,$$

$$\sum_{i\neq j}\langle 0|\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle=-75.2,$$

$$\langle 0|\nabla^2V|0\rangle=10.4\times10^4.$$

Since μ_{-2} and α are directly related by Eq. (2), and the only significant contributions to μ_{-2} are those of the discrete region and the 1.6–13 Ry region, it is possible to determine the discrete contribution from a knowledge of the other two quantities.

The discrete contributions to the other sum rules were determined by assigning 1.4 Ry as a mean energy $\bar{W}$ for the discrete region. Since the actual W's range only from 1.22 to 1.58 Ry, the above approximation contributes little error. The oscillator strength μ_{-2} (discrete) is then found by fitting the experimental value of α. Then μ_{-1} (discrete) $=\bar{W}\mu_{-2}$ (discrete); μ_0 (discrete) $=\bar{W}^2\mu_{-2}$ (discrete) $=0.26$. Cooper's calculation[18] of $2p-nd$, $2p-ns$ contributions to μ_0 gives 0.26. $2s-np$ transitions contribute[6] roughly 0.1 to the sum, with $1s-np$ transitions negligible. Thus there is reasonable agreement between the two estimates of the discrete contribution to μ_0.

Similarly, μ_1 (discrete) $=\bar{W}^3\mu_{-2}$ (discrete) $=0.4$ Ry, and μ_{-2} (discrete) is negligible.

Dalgarno and Kingston[19] have used measurements of the index of refraction and the Verdet constant for neon to obtain values for μ_{-2} and μ_{-1}. Our result for μ_{-2} is identical with theirs, since both are based on the same experimental data. They obtain $\mu_{-1}=1.925$ a.u., while our value is $\mu_{-1}=1.9$ with an error of about 5%.

The removal of $\sum_{j\neq k}\langle 0|\mathbf{r}_j\cdot\mathbf{r}_k|0\rangle$ from the sum total [see Eq. (7)] gives a diamagnetic susceptibility as computed from the sum rule of $-(7.05\pm0.50)\times10^{-6}$, as against Havens' value of $-(7.65\pm0.1)\times10^{-6}$.

The value of 10.3 ± 0.5 for the Thomas-Reiche-Kuhn rule agrees well with the expected theoretical value, $Z=10$. (This result was obtained earlier[1] by Ederer and Tomboulian.)

Using the value given above for $\sum_{i\neq j}\langle 0|\mathbf{p}_i\cdot\mathbf{p}_j|0\rangle$, Eq. (5) gives a sum rule value of $E_0=276\pm13$ Ry for the binding energy. The independent value is 257.88 ± 0.01 Ry.

The μ_2 value of $(11.2\pm0.6)\times10^4$ agrees with the value of $(10.4\pm1.0)\times10^4$ calculated from the Hartree-Fock wave functions.

The above results are summarized in Table II. We find reasonably good agreement between the quantities calculated from photoeffect data and those calculated from other experiments.

ACKNOWLEDGMENT

We are grateful to A. Bearden, H. Bethe, D. Ederer, E. McGuire, and D. Tomboulian for their assistance.

[13] G. G. Havens, Phys. Rev. **43**, 992 (1933).
[14] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).
[15] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), p. 153.
[16] W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. Edinburgh **62**, 37 (1944).
[17] Beatrice H. Worsley, Can. J. Phys. **36**, 289 (1958).
[18] J. W. Cooper, Phys. Rev. **128**, 681 (1962).
[19] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) **A259**, 424 (1960).