

## Radiative Corrections to the Energies of Atoms and Molecules\*

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A method for using sum rules in estimating the radiative corrections to the ground states of atoms and molecules is presented and applied to the ground states of hydrogen, helium, and lithium atoms, and the hydrogen molecule. The method appears capable of yielding energy shifts to accuracies of a few percent.

## I. INTRODUCTION

THE nonrelativistic part of the change in the energy level of an atomic system due to the interaction of the electrons with the vacuum electromagnetic field is given (see Ref. 1) in terms of the "mean excitation energy" defined by

$$nk_0 = \frac{\sum'_n \langle 0 | \mathbf{P} | n \rangle \cdot \langle n | \mathbf{p} | 0 \rangle (E_n - E_0) \ln |E_n - E_0|}{\sum'_n \langle 0 | \mathbf{P} | n \rangle \cdot \langle n | \mathbf{p} | 0 \rangle (E_n - E_0)}, \quad (1)$$

where the sum extends over the complete set of states of the system excluding the state in question. Evaluations of this quantity by explicit summation have been carried out for hydrogen<sup>2</sup> and helium.<sup>3-5</sup> These calculations are very sensitive to the description of the continuum contributions. The most accurate evaluations have been obtained by Schwartz,<sup>6,7</sup> using a perturbation-theory approach.

The above methods become increasingly intractable as the complexity of the atomic system increases, and the difficulties are compounded for molecular systems. An approximate method of evaluating (1) by use of the sum rules, essentially due to Dalgarno, is presented in Sec. II and applied to the ground states of hydrogen, helium, and lithium atoms and the hydrogen molecule.

## II. SUM-RULE METHOD

Dalgarno and Kingston<sup>8</sup> observed that the sum

$$S_p = \sum_j f_{0j} (E_j - E_0)^p, \quad (2)$$

where  $f_{0j}$  is the oscillator strength between states 0 and  $j$ , is a smooth function of  $p$ , the power of the energy. For ground states, the curve of  $S$  as a function of  $p$  exhibits a single minimum and is otherwise monotonic. In terms of the function (2), the expression for  $\ln k_0$

becomes

$$\ln k_0 = \frac{d}{dp} (\ln S_p) \Big|_{p=2}. \quad (3)$$

Thus, a knowledge of the functional form of  $S_p$  would suffice to determine  $\ln k_0$ . The same logarithmic derivative (3) evaluated at  $p=0$  gives the logarithm of  $I$ , the stopping power or average excitation energy for high-energy collisions. Reasonable accuracy has been achieved<sup>8</sup> in evaluating  $I$  using (3); the results are relatively insensitive to the actual functional form used, if both  $S_{-1}$  and  $S_1$  are known.

In general, four to seven values and a boundary condition on  $S$  as a function of  $p$  will be available: (a) With knowledge of an accurate ground-state wave function, sum rules furnish four points.<sup>9</sup> These are, in the fixed-nucleus approximation:

$$\begin{aligned} S_2 &= \frac{4}{3} \pi Z \langle 0 | \sum_i \delta^3(\mathbf{r}_i) | 0 \rangle, \\ S_1 &= \frac{2}{3} \langle 0 | (\sum_i \mathbf{p}_i)^2 | 0 \rangle, \\ S_0 &= n, \\ S_{-1} &= \frac{2}{3} \langle 0 | (\sum_i \mathbf{r}_i)^2 | 0 \rangle, \end{aligned} \quad (4)$$

(atomic units are used throughout unless otherwise specified). (b) The frequency-dependent polarizability of the system can be used to obtain more approximate data. That is, for long wavelengths the index of refraction can be written as a series<sup>8</sup>

$$\frac{n^2 - 1}{n^2 + 2} = C \sum_{m=1}^{\infty} \left( \frac{b}{\lambda^2} \right)^{m-1} S_{-2m}. \quad (5)$$

Precise measurements of the index of refraction can in practice yield as many as three additional points. [The static polarizability,  $\alpha(\omega=0) \equiv S_{-2}$ , is of course, separately determinable.] (c) Finally, the energy dependence of the continuum oscillator strengths provides a boundary condition<sup>3,4</sup> on  $S_p$  for ground states:  $S_{2.5} = \infty$ .

A possible functional form suggests itself from an examination of both discrete and continuum oscillator strengths for hydrogen and helium:

$$\begin{aligned} S_p &= D_1 (\Delta E_1)^p + D_2 (\Delta E_2)^p \\ &+ (E_I)^p \left( c_1 + c_5 p + \frac{c_2}{2.5 - p} + \frac{c_3}{3.0 - p} + \frac{c_4}{3.5 - p} \right), \end{aligned} \quad (6)$$

<sup>9</sup> See, for example, J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, in *Advances in Quantum Chemistry* (Academic Press Inc., New York, 1964), Vol. I.

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<sup>1</sup> H. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

<sup>2</sup> J. M. Harriman, *Phys. Rev.* **101**, 594 (1956).

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

<sup>4</sup> A. Dalgarno and W. Stewart, *Proc. Phys. Soc. (London)* **A76**, 49 (1960).

<sup>5</sup> E. E. Salpeter and A. Zaidi, *Phys. Rev.* **125**, 248 (1962).

<sup>6</sup> C. Schwartz and J. Tiemann, *Ann. Phys. (N. Y.)* **5**, 178 (1959).

<sup>7</sup> C. Schwartz, *Phys. Rev.* **123**, 1700 (1961).

<sup>8</sup> A. Dalgarno and A. E. Kingston, *Proc. Roy. Soc. (London)* **A259**, 424 (1960).

where  $\Delta E_i = E_i - E_0$  and  $E_I$  is the first ionization energy. The first two terms in (6) are the first two discrete state contributions to (3); the third and fourth term approximate the near continuum, and the last three terms correspond to a high-energy expansion of the continuum oscillator strength contributions. Here the  $D_i = f_{0i}$ , so that if the discrete oscillator strengths are known, the  $D_i$  need not be considered as variables. We note that for  $p$  large and negative the first term will dominate, and for positive  $p$  the terms corresponding to the continuum will dominate. The different portions of the spectrum are separately represented here; each part should be a positive, monotonic function of  $p$  in the region  $p = 2.5$  to  $-\infty$ .

As the number of electrons increases, the structure of the continuum oscillator strengths will change; the contributions corresponding to the  $K$ ,  $L$ ,  $M$ , etc. shells must be added to (6). The fact that  $S_p$  will still be a smooth function of  $p$  makes it plausible that moderately accurate  $\ln k_0$  values can be obtained by this method, even with only seven known  $S_p$  values. Of course, the prediction of  $I$  will be more accurate since the point at which the slope is desired is, in this case, at the center rather than at the edge of available accurate data.

The effect of multiply excited state contributions is not explicitly included in (6). Direct calculations of these contributions in helium<sup>4,5</sup> indicate that these states contribute  $\sim 0.3\%$  to  $\ln k_0$ , and  $S_p$  values. It is clear that the accuracy to which the  $S_p$  must be known increases in order to include these effects properly.

In considering this approximate method, we are guided by the direct evaluations of (1) which have been performed for the helium atom. In a limited sense, the extensive calculation of Dalgarno and Stewart<sup>4</sup> can be considered an application of this method, since they required their oscillator strengths to be consistent with the sum rules. It is noteworthy that their value of  $\ln k_0$  agrees better with the more exact value of Schwartz,<sup>7</sup> even though Salpeter and Zaidi<sup>5</sup> used the sum rule method to attempt a correction to their value. Pekeris<sup>10</sup> has used a power series fit to  $1/S_p$  for helium and obtained a value consistent with the four coefficient results given below.

Equation (6) and variants thereof have been tested on hydrogen and helium, where both  $I$  and  $\ln k_0$  are quite precisely known, and then applied to the hydrogen molecule and lithium atom ground states. These results are presented in the next section.

### III. RESULTS AND DISCUSSION

#### A. Hydrogen and Helium Atoms

Since in general only four and at best seven  $S_p$  values will be available, Eq. (6) was used in hydrogen and helium with four, five, and seven variable coefficients. The  $S_p$  values were taken in the order listed in Table I.

<sup>10</sup> C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

TABLE I. Ground state sums and oscillator strengths (atomic units).

	H	He	H <sub>2</sub>	Li
$S_2$	4	30.3325 <sup>b</sup>	3.69286 <sup>d</sup>	174.25 <sup>f</sup>
$S_1$	3	4.0837 <sup>b</sup>	1.70351 <sup>d</sup>	10.371 <sup>f</sup>
$S_0$	1	2	2	3
$S_{-1}$	2	1.505 <sup>b</sup>		12.322 <sup>f</sup>
$S_{-2}$	3	1.383 <sup>c</sup>	5.514 <sup>e</sup>	163 <sup>g</sup>
$S_{-4}$	26.5883 <sup>a</sup>	1.541 <sup>e</sup>	19.6 <sup>e</sup>	3.53 × 10 <sup>4g</sup>
$S_{-6}$	172.188 <sup>a</sup>	2.04 <sup>e</sup>	74.2 <sup>e</sup>	7.64 × 10 <sup>4g</sup>
$f_{01}$	0.42	0.27 <sup>b</sup>		0.75 <sup>h</sup>
$f_{02}$	0.08	0.08 <sup>b</sup>		0.006 <sup>h</sup>

<sup>a</sup> Reference 8.

<sup>b</sup> Reference 10.

<sup>c</sup> Reference 3.

<sup>d</sup> Reference 11.

<sup>e</sup> Reference 12.

<sup>f</sup> Reference 16.

<sup>g</sup> Predicted values (see text).

<sup>h</sup> Reference 17.

The results are presented in Table II, together with the "exact" values. It was found that the last three terms in (6) are all necessary to keep the  $S_p$  curve monotonic, but the accuracy is not at all affected by other combinations of choices. The accuracy was also not greatly affected by removal of the factor  $(E_I)^p$  from these last three terms, though the hydrogen values were in this case slightly above the correct result. Replacement of these last three terms by a power series in  $1/(2.5 - p)$  gave a slight improvement in helium ( $\ln k_0 = 4.34$ ), but worsened the hydrogen values ( $\ln k_0 = 2.80$ ). Other, more arbitrary, functional forms were used; all forms which yielded smooth  $S_p$  curves with the correct asymptotic behavior gave values within 10% of the correct values for  $\ln k_0$ . Of course,  $I$  was much more accurately predicted. Helium was found to be much less sensitive than hydrogen to functional form used.

#### B. Hydrogen Molecule

Since this is a two-electron system, (6) should provide reasonable values. The work of Kolos and Wolniewicz<sup>11</sup> gives sufficient information to obtain  $S_2$  and  $S_1$ , but the expectation value of  $\langle x_1 x_2 \rangle$ , needed for evaluating  $S_{-1}$ , is not given there. Dalgarno and Williams<sup>12</sup> have examined the index of refraction data and obtain  $S_{-2}$ ,  $S_{-4}$ ,  $S_{-6}$ . These values are all presented in Table I. Since the values of  $S_{-4}$  and  $S_{-6}$  are not very accurate, they have been used only to estimate  $f_{01}$  and  $f_{02}$ . We

TABLE II. Excitation energies for hydrogen and helium.

Method	Hydrogen		Helium	
	$I$ (eV)	$\ln k_0$ ( $k_0$ in Ry)	$I$ (eV)	$\ln k_0$ ( $k_0$ in Ry)
Exact	15.0 <sup>a</sup>	2.984 <sup>b</sup>	41.5 <sup>a</sup>	4.370 <sup>b</sup>
4-term	14.97	2.93	42.11	4.25
5-term	14.99	2.95	42.10	4.28
7-term	14.98	2.95	42.19	4.30

<sup>a</sup>Reference 8.

<sup>b</sup>References 6 and 7.

<sup>11</sup> W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).  
<sup>12</sup> A. Dalgarno and J. Williams, Proc. Phys. Soc. (London) **85**, 685 (1965).

note that for  $p \geq 0$ , the  $S_p(\text{H}_2)$  are approximately twice the  $S_p(\text{H})$ . (We mention in passing that the *average* dipole moments are the correct ones to use in obtaining the  $S_p$  needed here.)

Only a small range of values of  $f_{01}$  and  $f_{02}$  were found to be consistent with the  $S_p$  values in Table I. Variation within this range had very little effect on  $\ln k_0$  or on  $I$ . The results showed about the same sensitivity to functional form as the hydrogen values. The total spread of values obtained for  $\ln k_0$  was about 12%, and 2% for  $I$ . On the basis of these results we find for the hydrogen molecule<sup>13</sup>:

$$\begin{aligned} \ln k_0 &= 2.9 \pm 0.3 \quad (k_0 \text{ in Ry}), \\ I &= 19.5 \pm 0.5 \text{ eV}. \end{aligned}$$

We note that this  $\ln k_0$  value is very similar to that of the hydrogen atom, as was assumed without comment by Ladik.<sup>14</sup> The confidence limits on this result could probably be reduced by a factor of about 3 if  $S_{-1}$  were known. This result corresponds to a change in energy of the ground state of  $\text{H}_2$ —calculated by considering only the same diagrams as considered by Kabir and Salpeter<sup>6</sup>—of

$$\Delta E_0 = E_L(\text{H}_2) + E_L'(\text{H}_2),$$

where

$$\begin{aligned} E_L(\text{H}_2) &= (16/3)\alpha^3 \text{Ry} \langle 0 | \delta^3(\mathbf{r}_{1a}) + \delta^3(\mathbf{r}_{1b}) | 0 \rangle \\ &\quad \times [\ln(mc^2/k_0) + (19/30) - \ln 2] \\ &= 0.79 \pm 0.031 \text{ cm}^{-1}, \end{aligned}$$

$$E_L'(\text{H}_2) = (28/3)\alpha^3 \text{Ry} \langle 0 | \delta^3(\mathbf{r}_{12}) | 0 \rangle \ln \alpha = -0.033 \text{ cm}^{-1}.$$

This makes the radiative correction to the binding energy

$$\begin{aligned} \Delta D &= 2E_L(\text{H}) - \Delta E_0 \\ &= (0.54 - 0.76) \text{ cm}^{-1} = -0.22 \pm 0.03 \text{ cm}^{-1}. \end{aligned}$$

The experimental uncertainty which is quoted for the molecular ground state dissociation energy<sup>15</sup> reflects in

<sup>13</sup> This can be compared to  $I = 18.4$  eV given in Ref. 11. Dalgarno and Williams did not have the accurate values of Ref. 4 available to them.

<sup>14</sup> J. Ladik, J. Chem. Phys. **42**, 3340 (1965). A misprint of (3/16) for (16/3) which occurs in  $(E_2(\text{H}_2))$  both in this reference and in his original paper is apparently not used in the calculations.

<sup>15</sup> G. Herzberg and A. Monfils, J. Mol. Spectry. **5**, 482 (1960). I am grateful to Professor R. Bernstein for this observation.

part an averaging of two limiting atomic energy levels which could not be distinguished experimentally. The above result for the radiative correction, coupled with a sharpening of the work of Ref. 11, could reduce this uncertainty substantially.

### C. Lithium Atom

The expectation values calculated by Cooper and Martin<sup>16</sup> were used to obtain  $S_2$  through  $S_{-1}$  for the lithium ground state. Trumpy's self-consistent-field (SCF) values<sup>17</sup> for  $f_{01}$  and  $f_{02}$  are also listed in Table I.

Though only four  $S_p$  values do not provide sufficient latitude for adequately including the  $K$  shell terms in Eq. (6), we have nonetheless used it with the omission of the  $(E_I)^p$  factor from the last three terms. The power series form was also used. The total spread of  $\ln k_0$  values obtained was about 16%, somewhat larger than the previous cases. The results are

$$\begin{aligned} \ln k_0 &= 5.3 \pm 0.8 \quad (k_0 \text{ in Ry}), \\ I &= 33. \pm 3.5 \text{ eV}. \end{aligned}$$

While the spread of values does not permit much confidence in these values, they are consistent with the suggestion that the  $k_0$  for atoms is  $Z^2$  times that for hydrogen. This is quite well obeyed in helium as can be seen from Table I.

In passing we note that, using the  $f_{01}$ ,  $f_{02}$  given in Table I, the terms other than those from the first two excited states contribute only 8% to  $S_{-1}$ . If these oscillator strength values are accurate, we can predict  $S_{-2}$ ,  $S_{-4}$ ,  $S_{-6}$  using only the first two terms in (8):

$$S_{-2} = 163., \quad S_{-4} = 3.53 \times 10^4, \quad S_{-6} = 7.64 \times 10^6 \text{ (a.u.)}.$$

### ACKNOWLEDGMENTS

I am grateful to Professor S. T. Epstein for suggesting the problem, and to Professor C. Schwartz for helpful discussion.

<sup>16</sup> J. W. Cooper and J. B. Martin, Phys. Rev. **131**, 1183 (1963). Cooper (private communication) has advised us that his values of  $\sum_{i>j} \mathbf{r}_i \cdot \mathbf{r}_j$  and  $\sum_{i>j} \mathbf{p}_i \cdot \mathbf{p}_j$  are too large by a factor of 3. This change is reflected in Table I.

<sup>17</sup> B. Trumpy, Z. Physik **61**, 54 (1929).