6-1-1998

General Formulation of the Semirelativistic Approach to Atomic Sum Rules

P.T. Leung
Portland State University

Scott M. Cohen
Portland State University

Citation Details

Cohen, S. M., & Leung, P. T. (1998). General formulation of the semirelativistic approach to atomic sum rules. Physical Review A (Atomic, Molecular, And Optical Physics), 57(6), 4994-4997.

General formulation of the semirelativistic approach to atomic sum rules

S. M. Cohen and P. T. Leung
Department of Physics, Portland State University, P.O. Box 751, Portland, Oregon 97207-0751
(Received 3 November 1997; revised manuscript received 16 January 1998)

A general scheme is presented for obtaining systematic relativistic corrections to quantum-mechanical sum rules for various calculations in atomic physics. The single-particle picture and the Foldy-Wouthuysen transformation [Phys. Rev. **78**, 29 (1950)] are adopted to derive such corrections. Results are obtained for the ''generalized Bethe sums,'' which include all higher moments of the energy transfer, and explicit results are given to the lowest order of relativistic corrections.
[S1050-2947(98)04706-4]

PACS number(s): 34.50.Bw, 31.30.Jv, 11.55.Hx

I. INTRODUCTION

The problem of deriving relativistic corrections to the various quantum-mechanical sum rules has remained intriguing for the past 40 years, from the time it was studied in 1957 by Levinger and co-workers for the corrections to the Thomas-Reiche-Kuhn (TRK) sum rule [1–5]. Difficulties arise in attempting to extend nonrelativistic approaches to the relativistic case, for it is then necessary to sum over a set of final states that lacks the property of completeness due to the desired exclusion of all negative-energy states. It has nonetheless been important to pursue this problem due to the usefulness of these sum rules in the calculation of a number of integrated quantities related to atomic processes. Examples include the total photoabsorption cross sections and the energy loss of particles interacting with matter. Relativistic corrections to these sums will enable one to calculate these quantities to higher accuracy for heavy target atoms.

Conventionally, there have been at least three different approaches to this problem: (i) the projection operator method [2], (ii) the second quantization method [4], and (iii) the Foldy-Wouthuysen (FW) approach [1,5]. As is well known, the projection operator approach is mathematically complicated, even for the one-particle case. The second quantization method has to this point given merely formal (though rigorous) results, from which it is not yet clear how to analytically obtain numerical estimates for the relativistic correction terms. The FW approach, on the other hand, leads directly to quantitative results. Although the latter approach has been developed for one-particle systems only, the independent-particle, local-potential description for a many-electron atom allows one to generalize these one-particle results to obtain a first approximation to the corrections for many-particle systems [6,7]. This seemingly oversimplified picture has had some success in the literature in the analysis of x-ray scattering data using the TRK sum rule [6] and in the use of the Bethe sum rule to obtain corrections to the Bethe stopping power theory [7,8].

In the present work we give a consistent scheme using the FW transformation [9] to obtain relativistic corrections to the various ''generalized Bethe sums'' (defined below), which will be useful in the analysis of many atomic processes, such as those mentioned above [10]. We shall see that it is possible within this approach to obtain exact results for the simple case of a free relativistic electron, summing over the positive-energy states only. For bound atomic systems, expansions can be carried out that lead to order-by-order relativistic corrections. As we have pointed out above, this approach has been previously studied by many researchers [1,5]. Nonetheless, we believe our present formulation is more general in that (i) we do not limit ourselves to dipole transitions and (ii) we consider all higher-order moments of the energy transfer. In addition, we correct an inconsistency in several of the earlier works [1,5] with respect to the transformation of the ''multipole operator,'' as has been pointed out recently by Aucar, Oddershede, and Sabin [4]. Though our results are worked out for a one-electron system, the generalization to the many-particle case is understood in the sense described above, with further possible improvement discussed in the Conclusion. Explicit expressions are derived to the lowest relativistic corrections for all moments of the energy transfer, with the application of each indicated.

II. GENERAL FORMULATION

In this section we present a formulation for calculating relativistic sum rules. We wish to consider sum rules of the general form

$$S_k=\sum_l (E_l-E_n)^k|\langle l|A|n\rangle|^2$$

$$=\sum_l (E_l-E_n)^k\langle n|A^\dagger|l\rangle\langle l|A|n\rangle, \qquad (1)$$

where A will typically be related to the multipole operators, the sum is restricted to positive-energy eigenstates $|l\rangle$, and $|n\rangle$ is the initial state of the atom, usually taken to be the ground state. Note that if the $|l\rangle$ formed a complete set (as they do in the nonrelativistic case, but do not in the present one), the sum would immediately reduce to a form that is in general considerably easier to handle. To evaluate Eq. (1) further, let us first rewrite it as [11,12]

$$S_k=\sum_l \langle n|A^\dagger|l\rangle\langle l|A_k|n\rangle, \qquad (2)$$

with $A_k=[H,A_{k-1}]$, $A_0=A$, and H the Hamiltonian of the system under consideration. Defining the quantity [11]

$$S(\tau)=\sum_l \langle n|A^\dagger|l\rangle\langle l|e^{\tau H}Ae^{-\tau H}|n\rangle, \tag{3}$$

we have

$$S_k=\left.\frac{d^kS(\tau)}{d\tau^k}\right|_{\tau=0}. \tag{4}$$

The restriction to positive-energy states is conveniently carried out by introducing a Foldy-Wouthuysen transformation [9] through the operator e^{iU}. Then $S(\tau)$ becomes

$$S(\tau)=\sum_l \langle \hat{n}|\hat{A}^\dagger|\hat{l}\rangle\langle\hat{l}|e^{\tau\hat{H}}\hat{A}e^{-\tau\hat{H}}|\hat{n}\rangle, \tag{5}$$

where operators M transform into $\hat{M}=e^{iU}\,Me^{-iU}$, and $|\hat{l}\rangle=e^{iU}|l\rangle$. By construction, $\hat{H}$ contains no odd operators (those that connect positive- and negative-energy states), but $\hat{A}$ generally will. However, since $|\hat{l}\rangle$ and $|\hat{n}\rangle$ are both positive-energy states, these odd operators will not contribute and may thus be discarded. Since we are now dealing with a complete set of positive-energy states $|\hat{l}\rangle$, the sum leads directly to

$$S(\tau)=\langle\hat{n}|(e^{iU}A^\dagger e^{-iU})_{\mathcal{E}}e^{\tau\hat{H}}(e^{iU}Ae^{-iU})_{\mathcal{E}}e^{-\tau\hat{H}}|\hat{n}\rangle. \tag{6}$$

The subscript $\mathcal{E}$ indicates that we have discarded all odd parts of that operator enclosed within the parentheses. Equation (6), along with Eq. (4), represents a completely general formulation for calculating sums of the form of Eq. (1).

We now confine our attention to the generalized Bethe sum rules, for which

$$A=e^{i\vec{q}\cdot\vec{r}}, \tag{7}$$

for which $\vec{q}$ represents the momentum transfer to the atomic system. We then have for any operator $M(\vec{p})$, with $\vec{p}$ the momentum operator,

$$\begin{aligned} M(\vec{p})A&=AM(\vec{p}+\hbar\vec{q})\equiv AM_q,\\ A^\dagger M(\vec{p})&=M(\vec{p}+\hbar\vec{q})A^\dagger\equiv M_qA^\dagger. \end{aligned} \tag{8}$$

Note that these relations remain true when $M(\vec{p})$ is also a function of the position coordinate $\vec{r}$ at least as long as $M(\vec{p})$ has a Taylor series expansion in powers of $\vec{p}$. Since both $\hat{H}$ and U satisfy this requirement, we may apply Eq. (8) to Eq. (6) to obtain

$$S(\tau)=\langle\hat{n}|(e^{iU}e^{-iU_q})_{\mathcal{E}}e^{\tau\hat{H}_q}(e^{iU_q}e^{-iU})_{\mathcal{E}}e^{-\tau\hat{H}}|\hat{n}\rangle. \tag{9}$$

Using Eq. (4), we present three equivalent forms for $S_k=S_k(\vec{q})$:

$$\begin{aligned} S_k(\vec{q})&=\langle\hat{n}|R^\dagger[\hat{H},[\hat{H},\cdots[\hat{H},R]_q\cdots]_q]_q|\hat{n}\rangle\\ &=\sum_{j=0}^{k}(-1)^j\binom{k}{j}\langle\hat{n}|R^\dagger\hat{H}_q^{k-j}R\hat{H}^j|\hat{n}\rangle\\ &=\langle\hat{n}|R^\dagger(\hat{H}_q-E_n)^kR|\hat{n}\rangle, \end{aligned} \tag{10}$$

with k pairs of commutator brackets and $\binom{k}{j}$ the binomial coefficients. Here

$$R=(e^{iU_q}e^{-iU})_{\mathcal{E}} \tag{11}$$

and our modified commutator is defined as

$$[M,\mathcal{O}]_q\equiv M_q\mathcal{O}-\mathcal{O}M. \tag{12}$$

For the purpose of calculating explicit values for these sums, the final form in Eq. (10) is often easiest.

To this point, no approximations have been made in deriving these equations. To proceed further in calculating $S_k(\vec{q})$, it is generally necessary to first specify a Hamiltonian and then to use a semirelativistic approach by expanding the various operators in powers of m^{-1} (that is, in powers of v^2/c^2). It is interesting to note, however, that in the case of a free Dirac particle it is possible to obtain exact results for all k. We have in this case

$$H=\beta mc^2+c\vec{\alpha}\cdot\vec{p}, \tag{13}$$

with β and α_i the usual Dirac matrices, and [9]

$$e^{\pm iU}=\left[\frac{E_p+mc^2}{2E_p}\right]^{1/2}\pm\frac{\beta\vec{\alpha}\cdot\vec{p}}{p}\left[\frac{E_p-mc^2}{2E_p}\right]^{1/2}. \tag{14}$$

This leads to

$$\hat{H}=E_p=\sqrt{m^2c^4+p^2c^2} \tag{15}$$

and

$$\begin{aligned} R=&\left[\frac{E_p+mc^2}{2E_p}\right]^{1/2}\left[\frac{E_{p'}+mc^2}{2E_{p'}}\right]^{1/2}\\ &+\frac{\vec{\alpha}\cdot\vec{p}'\,\vec{\alpha}\cdot\vec{p}}{pp'}\left[\frac{E_p-mc^2}{2E_p}\right]^{1/2}\left[\frac{E_{p'}-mc^2}{2E_{p'}}\right]^{1/2}, \end{aligned} \tag{16}$$

where $\vec{p}'=\vec{p}+\hbar\vec{q}$. Note that we have dropped the odd terms, according to our definition of R. Now all the operators in Eq. (10) commute with each other, so we obtain

$$S_k(\vec{q})=R^\dagger R(E_{p_n'}-E_{p_n})^k. \tag{17}$$

Here $R^\dagger R$ may be obtained from Eq. (16) as

$$R^\dagger R=\frac{1}{2}+\frac{E_p}{2E_{p'}}+\frac{\hbar c^2\vec{q}\cdot\vec{p}}{2E_pE_{p'}} \tag{18}$$

and it is understood in this expression that all quantities are evaluated at $\vec{p}=\vec{p}_n$, with $\vec{p}_n$ the momentum of the initial state $|\hat{n}\rangle$ (which is here an eigenstate of momentum and therefore $R^\dagger R$ as well as energy). We stress that this result is exact and only positive-energy states have been included in

the sum. It will be useful as a limiting case to check relativistic calculations of these sum rules for bound particles.

For nonrelativistic velocities, exact results for these sum rules may be obtained, even for the case of a bound particle [13]. In the appropriate limit, Eq. (17) leads to results in agreement with these nonrelativistic sums. For relativistic velocities, however, only the free particle case can be done exactly. For bound particles, it is necessary to use approximate methods, as we illustrate in the next section.

III. EXPLICIT RESULTS FOR $S_k(\vec{q})$

Let us now apply our results to the generalized Bethe sum rules for a relativistic bound particle and any k. In the following, all of our results will be found to $O(m^{-3})$. From Eq. (10) we have

$$S_k(\vec{q})=\langle\hat{n}|R^{\dagger}(\hat{H}_q-E_n)^k R|\hat{n}\rangle, \tag{19}$$

where

$$\hat{H}=mc^2+\frac{p^2}{2m}+eV(\vec{r})-\frac{p^4}{8m^3c^2}-\frac{e\hbar}{4m^2c^2}\,\vec{\sigma}\cdot(\vec{E}\times\vec{p}) -\frac{e\hbar^2}{8m^2c^2}\,\vec{\nabla}\cdot\vec{E} \tag{20}$$

and $\vec{E}=-\vec{\nabla}V(\vec{r})$. Using the results for e^{iU} from the FW transformation theory [9], we obtain from Eq. (11)

$$R=1-\frac{\hbar^2q^2-2i\hbar\vec{\sigma}\cdot(\vec{q}\times\vec{p})}{8m^2c^2}-\frac{ie\hbar^2\vec{q}\cdot\vec{E}}{4m^3c^4}, \tag{21}$$

with $R^{\dagger}=R|_{q\to -q}$. Note that in the low-q limit, Eq. (21) agrees with the previous result obtained for the dipole operator [2]. Inserting Eq. (21) into Eq. (19), we obtain

$$S_k(\vec{q})=\left(1-\frac{\hbar^2q^2}{4m^2c^2}\right)\langle\hat{n}|(\hat{H}_q-E_n)^k|\hat{n}\rangle +\frac{i\hbar}{4m^2c^2}\,\langle\hat{n}|[(\hat{H}_q-E_n)^k,\vec{\sigma}\cdot(\vec{q}\times\vec{p})]|\hat{n}\rangle. \tag{22}$$

This expression may be evaluated in a straightforward way. We list below our results for $S_k(\vec{q})=S_k^{\mathrm{NR}}(\vec{q})+\Delta S_k(\vec{q})$, where $S_k^{\mathrm{NR}}(\vec{q})$ is equal to the nonrelativistic limit of $S_k(\vec{q})$ and $\Delta S_k(\vec{q})$ is its relativistic correction. We also present the corresponding dipole sum rules, which are given by Eq. (1) with $A=\vec{r}$ and which we denote by S_k^d. Apart from the case $k=0$, which must be calculated directly, these sums may be obtained from our results for $S_k(\vec{q})$ via the expression $S_k^d=\frac{1}{2}\nabla_q^2 S_k(\vec{q})|_{q=0}$.

A. Case $k=0$

This sum follows directly from Eq. (22). It is related to the total cross section for scattering of an incident ion by atomic electrons [10]. We find

$$\begin{aligned} S_0(\vec{q})&=1+\Delta S_0(\vec{q}),\\ \Delta S_0(\vec{q})&=-\frac{\hbar^2q^2}{4m^2c^2},\\ S_0^d&=\langle\hat{n}|r^2|\hat{n}\rangle+\Delta S_0^d,\\ \Delta S_0^d&=-\frac{i\hbar^2}{2m^2c^2}\,\langle\hat{n}|\vec{\sigma}\cdot(\vec{r}\times\vec{\nabla})|\hat{n}\rangle-\frac{e\hbar^2}{2m^3c^4}\,\langle\hat{n}|\vec{r}\cdot\vec{E}|\hat{n}\rangle. \end{aligned} \tag{23}$$

The dipole sums in this case follow from [see Eq. (6)]

$$S_k^d=\langle\hat{n}|(e^{iU}\vec{r}e^{-iU})_{\mathcal{E}}\cdot(e^{iU}\vec{r}e^{-iU})_{\mathcal{E}}|\hat{n}\rangle, \tag{24}$$

and the fact that

$$(e^{iU}\vec{r}e^{-iU})_{\mathcal{E}}=\vec{r}-\frac{\hbar}{4m^2c^2}\,\vec{\sigma}\times\vec{p}-\frac{e\hbar^2}{4m^3c^4}\,\vec{E}. \tag{25}$$

B. Case $k=1$

We would like to point out that for the case $k=1$, if we expand Eq. (17) in powers of m^{-1}, we find a discrepancy when compared to the free-particle limit of previous results [5]. Aucar, Oddershede, and Sabin [4] have noted that there is an inconsistency in the treatment of the operator A in Ref. [5]. There (and in several other treatments of the less general TRK sum rule [1]), the FW transformation of A has been neglected. According to our present formalism, this problem is corrected.

This sum, which is related to the average energy transfer in scattering processes and to the electronic stopping power of materials [10], is also straightforward to calculate from Eq. (22). Using the fact that

$$(\hat{H}_q-E_n)|\hat{n}\rangle=(\hat{H}_q-\hat{H})|\hat{n}\rangle, \tag{26}$$

where

$$(\hat{H}_q-\hat{H})=\frac{\hbar^2q^2}{2m}+\frac{\hbar\vec{q}\cdot\vec{p}}{m}+\frac{e\hbar^2}{4m^2c^2}\,\vec{\sigma}\cdot(\vec{q}\times\vec{E}), \tag{27}$$

along with some simple manipulations, we obtain

$$\begin{aligned} S_1(\vec{q})&=\frac{\hbar^2q^2}{2m}+\Delta S_1(\vec{q}),\\ \Delta S_1(\vec{q})&=-\frac{\hbar^4q^4}{4m^3c^2}+\frac{\hbar^4q^2}{4m^3c^2}\,\langle\hat{n}|\nabla^2|\hat{n}\rangle +\frac{\hbar^4}{2m^3c^2}\,\langle\hat{n}|(\vec{q}\cdot\vec{\nabla})^2|\hat{n}\rangle,\\ S_1^d&=\frac{3\hbar^2}{2m}+\Delta S_1^d,\\ \Delta S_1^d&=\frac{5\hbar^2}{4m^3c^2}\,\langle\hat{n}|\nabla^2|\hat{n}\rangle. \end{aligned} \tag{28}$$

The result for $S_1(\vec{q})$ is identical to that of Ref. [5] except for the fact that the q^4 term is here twice as large, the difference

being due to the transformation of the operator A. Note that since the dipole (TRK) sum rule is given solely by the q^2 parts of this expression, the transformation of the operator A does not affect those results [2].

C. Case $k=2$

The sum $S_2(\vec{q})$ gives the width of the straggling function [10], which is the probability distribution of energy loss in collisions. This calculation is simplified by noting that for $k=2$ we may still use the relation $\langle\hat{n}|(\hat{H}_q-E_n)^k|\hat{n}\rangle = \langle\hat{n}|(\hat{H}_q-\hat{H})^k|\hat{n}\rangle$ (but note carefully that for $k\geq 3$, this equality does not hold due to the fact that $[\hat{H}_q,\hat{H}]\neq 0$). We find

$$
\begin{aligned}
S_2(\vec{q}) &= \frac{\hbar^4 q^4}{4m^2} - \frac{\hbar^2}{m^2}\langle\hat{n}|(\vec{q}\cdot\vec{\nabla})^2|\hat{n}\rangle + \Delta S_2(\vec{q}),\\
\Delta S_2(\vec{q}) &= -\frac{ie\hbar^4}{m^3c^2}\langle\hat{n}|\vec{\sigma}\cdot(\vec{q}\times\vec{E})\vec{q}\cdot\vec{\nabla}|\hat{n}\rangle\\
&\quad -\frac{ie\hbar^4}{2m^3c^2}\langle\hat{n}|[\vec{q}\cdot\vec{\nabla}\vec{\sigma}\cdot(\vec{q}\times\vec{E})]|\hat{n}\rangle,\\
S_2^d &= -\frac{\hbar^4}{m^2}\langle\hat{n}|\nabla^2|\hat{n}\rangle + \Delta S_2^d,\\
\Delta S_2^d &= \frac{ie\hbar^4}{m^3c^2}\langle\hat{n}|(\vec{\sigma}\times\vec{E})\cdot\vec{\nabla}|\hat{n}\rangle + \frac{ie\hbar^4}{2m^3c^2}\langle\hat{n}|\vec{\nabla}\cdot(\vec{\sigma}\times\vec{E})|\hat{n}\rangle.
\end{aligned}
\tag{29}
$$

Notice here that due to the presence of the spin operator $\vec{\sigma}$, $\Delta S_2(\vec{q})$ depends on the orientation of the spin relative to the direction of the momentum transfer $\vec{q}$. For a central potential, $V(\vec{r})=V(r)$, ΔS_2^d vanishes to $O(m^{-3})$ for all spherically symmetric states. To avoid confusion, we would like to point out that the gradients in the last terms of $\Delta S_2(\vec{q})$ and ΔS_2^d operate on $\vec{E}$ only and not on the ket $|\hat{n}\rangle$.

D. Case $k=3$

The sum $S_3(\vec{q})$ gives the skewness or degree of asymmetry of the straggling function [10]. Our results are

$$
\begin{aligned}
S_3(\vec{q}) &= \frac{e\hbar^4}{m^2}\langle\hat{n}|\vec{q}\cdot\vec{E}\vec{q}\cdot\vec{\nabla}|\hat{n}\rangle + \frac{\hbar^6 q^6}{8m^3} - \frac{3\hbar^4 q^2}{2m^3}\langle\hat{n}|(\vec{q}\cdot\vec{\nabla})^2|\hat{n}\rangle,\\
\Delta S_3(\vec{q}) &= 0,\\
S_3^d &= -\frac{e\hbar^4}{2m^2}\langle\hat{n}|(\vec{\nabla}\cdot\vec{E})|\hat{n}\rangle,\\
\Delta S_3^d &= 0.
\end{aligned}
\tag{30}
$$

Note that to $O(m^{-3})$, it can be shown that $\Delta S_k(\vec{q})$ vanishes for all $k\geq 3$.

IV. CONCLUSION

We have demonstrated that relativistic corrections to the various generalized oscillator strength sum rules can be effectively obtained from the Foldy-Wouthuysen approach. Although a rigorous second quantization formulation has been available [4], the practical application of the results from this formulation to actual atomic calculations has yet to be explored. On the other hand, our present approach enables one to make estimates for the case of many-electron atoms in a straightforward manner under the independent-particle, local-potential approximation [6]. In addition, it may be possible to improve the present approach by adopting an effective Hamiltonian (e.g., the Dirac-Hartree-Fock Hamiltonian) for the target atoms and to apply the FW scheme to this case. Further development on the many-electron results and its application to stopping power calculations will be left for future work.

ACKNOWLEDGMENT

Partial support from the Faculty Development Committee of Portland State University is acknowledged.

[1] J. S. Levinger, M. L. Rustgi, and K. Okamoto, Phys. Rev. **106**, 1191 (1957); H. O. Dogliani and W. F. Bailey, J. Quant. Spectrosc. Radiat. Transf. **9**, 1643 (1969); T. Matsuura and K. Yazaki, Phys. Lett. **46B**, 17 (1973); J. L. Friar and S. Fallieros, Phys. Rev. C **11**, 274 (1975).

[2] K.-M. Schmitt and H. Arenhövel, Z. Phys. A **320**, 311 (1985).

[3] S. P. Goldman and G. W. F. Drake, Phys. Rev. A **25**, 2877 (1982).

[4] G. A. Aucar, J. Oddershede, and J. R. Sabin, Phys. Rev. A **52**, 1054 (1995).

[5] P. T. Leung, M. L. Rustgi, and S. A. T. Long, Phys. Rev. A **33**, 2827 (1986).

[6] D. Y. Smith, Phys. Rev. A **35**, 3381 (1987).

[7] P. T. Leung, Phys. Rev. A **40**, 5417 (1989).

[8] H. Bichsel, Phys. Rev. A **46**, 5761 (1992); J. Mompart, C. Domingo, C. Baixeras, and F. Fernandez, Nucl. Instrum. Methods Phys. Res. B **107**, 56 (1996).

[9] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[10] See also H. Bichsel, in *Atomic, Molecular, and Optical Physics Handbook*, edited by G. W. F. Drake (AIP, New York, 1996), p. 1032.

[11] R. Jackiw, Phys. Rev. **157**, 1220 (1967).

[12] H. A. Bethe and R. W. Jackiw, *Intermediate Quantum Mechanics*, 2nd ed. (Benjamin, New York, 1968), Chap. 11.

[13] See Ref. [12]. It is interesting to note that for the Bethe sum rule ($k=1$), the nonrelativistic sums for both the free and the bound particles are identical.