Subshell formula for the Bethe-Born stopping approximation

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It is known that the subshell contributions to the coefficient of the $O(\ln E)$ asymptotic term of the Bethe-Born stopping-number formula are not given correctly by partitioning the squared matrix element defining this coefficient into a simple sum of its subshell contributions. This interesting result is extended to the second, or $O(1)$, asymptotic term in the stopping number. In this case, the subshell decomposition results in a sum of two expressions. One is simply the subshell decomposition of the squared matrix element defining the $O(1)$ coefficient for the total system. The second term is more complex in form but sums to zero, as it must, when summed over all subshells in the target. It is pointed out that this second term and its summation requirement can be used to impose a useful restriction on the construction of theoretical subshell corrections for the Bethe-Born formula.

The Bethe-Born approximation to the stopping number B of a structureless charged particle incident on an atomic target,[1]

$$B \sim (Z-q)\ln(4mE/MR) - L(0) , \tag{1}$$

is extremely useful because of its simplicity. Equation (1) is the first two terms in the asymptotic expansion of the stopping number for large collision energies E. Here, $Z-q$ is the number of electrons bound to a target with nuclear charge Z, q is the ionic charge of the target, m is the electron mass, and M is the projectile mass. The quantity

$$L(0) = \sum_j f_j \ln(\Delta E_j / R) \tag{2}$$

poses the only requirement for detailed information concerning the target structure. The sum in Eq. (2) is over all target electronic states, including the continuum, f_j is the dipole oscillator strength, ΔE_j is the target's transition energy between the initial and jth states, and R is the Rydberg energy unit.

The two coefficients $Z-q$ and $L(0)$ appearing in Eq. (1) have been partitioned into their subshell contributions for a number of purposes. This included the important problem of constructing shell corrections to the Bethe-Born formula (see Ref. 2, for example) and facilitating the indirect computation[3] of $L(0)$. The subshell decomposition of the $O(\ln E)$ coefficient is intuitively expected to be

$$Z-q = S(0) \simeq \sum_n S_n(0) ,$$

where $S(0)$ equals the target's dipole-oscillator-strength sum over all states as defined by the Thomas-Kuhn sum rule.[1,4] $S_n(0)$ is the analogous sum for some subset of occupied target states that are considered equivalent, such as a shell or subshell. However, it was shown in Ref. 5 that this expectation is not correct and a more general form for this partitioning is required. Shell-correction terms have been computed by a number of investigators,[6] but a general formula for the $O(1)$ coefficient in Eq. (1) was not displayed in these works.

The following discussion presents an extension of the Ref. 5 results to the coefficient of the $O(1)$ term in Eq. (1), $L(0)$. This coefficient is demonstrated to have terms in addition to those that make up the shell, or subshell, contributions to $L(0)$. These additional terms in the subshell formula for the coefficient of $O(1)$ sum to zero when summed over all occupied orbitals. This is, of course, necessary if Eq. (1) is to be recovered. This requirement results in an important restriction on the construction of shell corrections for the Bethe-Born stopping number.

All theories that attempt the construction of a shell, or subshell, correction to the stopping number reduce the matrix elements required in this computation to one-electron form.[1-3,5-7] This is justified if wave functions of the Hartree-Fock type are used to describe the target (i.e., electron correlation is ignored) and if the one-electron orbitals in this wave function are orthonormal. Hence a one-electron theory is assumed here in extending the results presented in Ref. 5. However, the following presentation differs in two ways from that given in Ref. 5. A target with fully occupied orbitals is assumed in Ref. 5. This specialization is avoided here by the introduction of a factor constructed to preserve the Thomas-Kuhn sum rule for arbitrary orbital occupation and to reduce to the fully-occupied-orbital cases treated in Refs. 5 and 7. This factor has not been derived by starting with a Hartree-Fock-type

multielectron wave function and must be considered *ad hoc* in origin. The second difference concerns the assumption made here that the target orbitals are members of the same orthonormal and complete set. Satisfaction of the Thomas-Kuhn sum rule is guaranteed by this assumption. However, the following developments do not depend on this assumption, and they apply to as broad a class of one-electron orbitals as do the results of Ref. 5.

Here, the target is described by a single complete set of orthonormal orbitals $\psi_\alpha(\tau)$ that could have been generated, for example, in a Hartree or Hartree-Fock-Slater treatment of the target. In a nonrelativistic treatment, the collective index α indicates the principal, the total angular momentum (l), the angular momentum projection (m), and the spin-projection (μ) quantum numbers. The orbitals are degenerate in m and μ, so the natural choice for an equivalent set of electrons would be those with the same principal and total angular momentum quantum numbers. This set has a degeneracy $d=2(2l+1)$, and its occupation is p. Subscripts are added to these quantities to distinguish sets of equivalent electrons. The one-electron matrix element basic to stopping power is related to the dimensionless generalized oscillator strength

$$\phi(K;i,n)=[4\Delta E(i,n)m/(\hbar^2K^2d_n)]\sum_{\substack{m_i\\ \mu_i}}\sum_{\substack{m_n\\ \mu_n}}\left|\int d\tau\,\psi^*_{\alpha i}(\tau)\psi_{\alpha n}(\tau)\exp(i\vec{K}\cdot\vec{r})\right|^2 . \tag{3}$$

Here, $n(i)$ designates the principal and total angular momentum quantum numbers for the initial (final) set of equivalent electrons, $\Delta E(i,n)$ is the energy difference between the n and i orbitals, and $\vec{K}$ is the usual momentum transfer.[1] The one-electron dipole oscillator strength is $\phi(0;i,n)$.

All matrix elements required to describe the target stopping are constructed from the one-electron quantity introduced in Eq. (3). For example, the stopping number for the set of equivalent electrons described by the index n is written here as

$$B_n=p_n\sum_i(1-h_i)\int_{K_s(i,n)}^{K_l(i,n)}dK\,K^{-1}\phi(K;i,n) , \tag{4}$$

where K_s (K_l) is the minimum (maximum) value for the momentum transfer and $h_i=p_i/d_i$. The sum, as are all sums appearing below, is over all i values needed to define the complete set ψ_α, including the continuum. The sum of B_n, defined in Eq. (4), over all n is the present one-electron approximation to B of Eq. (1). Other many-electron quantities required below are written in an analogous fashion as

$$S_n(0)=p_n\sum_i(1-h_i)\phi(0;i,n) \tag{5}$$

and

$$L_n(0)=p_n\sum_i(1-h_i)\phi(0;i,n)\ln[\Delta E(i,n)/R] . \tag{6}$$

The sum of Eq. (5) over n is shown below to be consistent with the Thomas-Kuhn sum rule, mentioned above, and the same sum over Eq. (6) is the present approximation to $L(0)$ appearing in Eqs. (1) and (2). Note that the above definitions also provide the one-electron sum rule

$$\sum_i\phi(K;i,n)=1 \tag{7}$$

and the approximations

$$\begin{aligned} &K_l(i,n)\sim 2mM^{-1}k ,\\ &K_s(i,n)\sim M\,\Delta E(i,n)/(\hbar^2k), \end{aligned} \tag{8}$$

apply if $E=\hbar^2k^2/2M\gg\Delta E(i,n)$.

The idea of a partial sum rule appears to have been first introduced in Ref. 7. The Ref. 7 work and its subsequent application in Ref. 5 assume all degenerate orbitals are either full or empty. The $(1-h_i)$ term is introduced here to avoid this restriction and, as it was constructed from the requirements that (a) the present one-electron model reproduce the Thomas-Kuhn sum rule for the atom and (b) it reproduce the full or empty ($h_i=1$ and 0, respectively) degenerate orbital results.

Elementary concepts from distribution theory[8] can be used to express B_n in a form more convenient for the following asymptotic developments. Equation (4) can be rewritten as

$$\begin{aligned} B_n&=p_n\sum_i(1-h_i)\int_{t_s(i,n)}^{t_l(i,n)}dt\,t^{-1}\phi(t;i,n)\\ &=p_n\sum_i(1-h_i)\lim_{\epsilon\to0}\left[\int_\epsilon^{t_l(i,n)}dt\,t^{-1}\phi(t;i,n)+\phi(0;i,n)\ln\epsilon-\int_\epsilon^{t_s(i,n)}dt\,t^{-1}\phi(t;i,n)-\phi(0;i,n)\ln\epsilon\right] , \end{aligned} \tag{9}$$

where the change of variable $t=\hbar K(2mR)^{-1/2}$ was introduced for later convenience. The definition of the fin-

ite part of a divergent integral,[8] if $\phi(t;i,n)$ satisfies some relatively weak restrictions, is

$$Fp\int_0^{t_l(i,n)} dt\, t^{-1}\phi(t;i,n)=\lim_{\epsilon\to 0}\left[\int_\epsilon^{t_l(i,n)} dt\, t^{-1}\phi(t;i,n)+\phi(0;i,n)\ln\epsilon\right],$$

so Eq. (9) becomes

$$B_n=p_n\sum_i(1-h_i)\left[Fp\int_0^{t_l(i,n)} dt\, t^{-1}\phi(t;i,n)-Fp\int_0^{t_s(i,n)} dt\, t^{-1}\phi(t;i,n)\right]. \tag{10}$$

The manipulations used[5,7] to develop a large-E asymptotic expression for Eq. (10) requires interchanges of the $\sum_i$ operation, which allows $\Delta E(i,n)$ to approach infinity, the dt integration, and the limit as E approaches infinity. A rather long but elementary argument using the techniques of Ref. 9 can be used to construct conditions on $\phi(t;i,n)$ that guarantee no asymptotic error of order $O(1)$ occurs in making these interchanges. Such conditions certainly exist, and this point is dismissed with the assumption that a realistic generalized oscillator strength will also conform to these conditions. Neither Ref. 5 nor 7 discusses these questions.

The expansion[4] for small t

$$\phi(t;i,n)=\phi(0;i,n)+a(i,n)t^2+\cdots,$$

where a is independent of t, provides the result

$$\lim_{E\to\infty}\left[Fp\int_0^{t_s(i,n)} dt\, t^{-1}\phi(t;i,n)-Fp\int_0^{t_s(i,n)} dt\, t^{-1}\phi(0;i,n)\right]=O(E^{-1})$$

if $\Delta E(i,n)$, appearing in the definition of $t_s(i,n)$, has any finite value. If this stipulation about $t_s(i,n)$ is ignored, as effected by the interchange of operations discussed in the previous paragraph, one may rewrite Eq. (10) as

$$B_n\sim p_n\sum_i(1-h_i)\left[Fp\int_0^{t_l(i,n)} dt\, t^{-1}\phi(t;i,n)-\phi(0;i,n)\ln t_s(i,n)\right]. \tag{10'}$$

The integration limit $t_l(i,n)$ appearing in Eq. (10') is independent of i if Eq. (8) is used, so the integration and summations operations can be interchanged, and

$$B_n\sim p_nFp\int_0^{t_l} dt\, t^{-1}-p_n\sum_i(1-h_i)\phi(0;i,n)\ln t_s(i,n)-p_n\sum_i h_iFp\int_0^{t_l} dt\, t^{-1}\phi(t;i,n)$$

$$\sim p_n\ln t_l-p_n\sum_i(1-h_i)\phi(0;i,n)\ln t_s(i,n)-p_n\sum_i h_iFp\int_0^{t_l} dt\, t^{-1}\phi(t;i,n)$$

results if Eq. (7) is used. Finally, the definitions of Eqs. (5)—(8) provide

$$B_n\sim[p_n+S_n(0)]\ln[\hbar kM^{-1}(2m/R)^{1/2}]-L_n(0)$$
$$-p_n\sum_i h_iFp\int_0^{t_l} dt\, t^{-1}\phi(t;i,n). \tag{11}$$

The coefficient of the $O(\ln E)$ [$=O(\ln k)$] term is identical to that found in Ref. 5. The definition of Fp is provided between Eqs. (9) and (10).

Equation (11) is an asymptotic representation of the Born stopping number including all $O(\ln E)$ and $O(1)$ terms for the equivalent electrons described by n. Equation (1) must be recovered when summed over all orbitals in the complete set describing the target.

The required properties become obvious by use of the general relationship between the oscillator strength for the j-k and k-j transitions[10]

$$d_j\phi(K;k,j)=-d_k\phi(K;j,k), \tag{12}$$

which is satisfied here [see Eq. (3)]. For any nonzero contribution to the sum

$$\sum_n\sum_i p_nh_i\phi(K;i,n)=\sum_n\sum_i(p_np_i/d_i)\phi(K;i,n), \tag{13}$$

say $i=k$ and $n=j$, there must be another term with indices reversed. Equation (12) shows that this pair of terms sums to zero, and hence Eq. (13) also equals zero. This is sufficient to show that the sum of Eq. (5) over n reproduces the Thomas-Kuhn sum rule. Hence

$$Z-q=S(0)=\sum_n S_n(0)=\tfrac{1}{2}\sum_n[S_n(0)+p_n]$$

and the $O(\ln E)$ coefficient in Eq. (1) is obtained from Eq. (11). The same argument shows that the term following $L_n(0)$ in Eq. (11), i.e., the third term, sums to zero as required. Note that t_l is independent of summation variables i and n. Finally, the n sum of Eq. (11) equals B of Eq. (1) if the Eq. (6) def-

inition is used.

The form presented in Eq. (11) for the orbital contribution to the Bethe-Born stopping number is new, and the existence of the third term in Eq. (11) has been implicitly ignored on occasion when discussing shell corrections; see Ref. 11 for an example. In fact, this third term imposes an important restriction on the construction of shell corrections. To derive a shell correction from theory for a particular set of equivalent electrons, it is necessary to have a low-energy theory that is accurate at sufficiently large E to overlap the small-E range of validity for Eq. (11). If the relatively easy-to-calculate quantities S_n and $L_n(0)$ are known,[3] then a value for the third term of Eq. (11) is also known. When this process is carried out for all sets of equivalent electrons, the resulting n and sum of Eq. (11) must revert to Eq. (1). This requires the numerical values for the third term just generated to sum to zero. If the low-energy and Bethe-Born theories describe the same process to the same degree of accuracy, this requirement should be satisfied. The present use of Bethe-Born theory is generally accepted as accurate, so if this requirement is not satisfied, the low-energy theory can be renormalized to produce the required result. This procedure has been carried out for proton stopping[12] with encouraging results.

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