Shannon entropies and logarithmic mean excitation energies from cusp- and asymptotic-constrained model densities

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A model correctly describing the asymptotic behavior of the charge density is used to derive an expression for the Shannon entropy in terms of the ionization potential of the system. A strong similarity is observed between this model entropy and the entropy obtained from correlated wave functions providing evidence that it is the asymptotic regions that are responsible for the behavior of the entropy. We also show via a model entropy that the behavior of the momentum space Shannon entropy is due to a correct description of the cusp behavior at the nucleus. The changes in the position and momentum space entropies as a function of a parameter are shown to be linearly related for these models. The expression for the entropy, derived from a density model that obeys the asymptotic behavior, is shown to be almost identical in nature to the general expression for entropy emanating in the stopping power formalism.

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I. INTRODUCTION

Information entropies such as Shannon have enjoyed wide application in several disciplines [1]. These quantities are of interest as measures of the extent, spread, or *shape* of the underlying distribution from which they are derived. Shannon entropy [2] of the charge density may be defined as

$$S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}, \tag{1.1}$$

and of the momentum space density $\pi(\mathbf{p})$ as

$$S_\pi = -\int \pi(\mathbf{p}) \ln \pi(\mathbf{p}) d\mathbf{p}. \tag{1.2}$$

Shannon entropy measures the delocalization or the lack of structure in the respective distribution. Thus S_ρ is maximal for a uniform distribution, for example, that of an unbound system, and is minimal when the uncertainty about the structure of the distribution is minimal, e.g., a delta-like distribution. S_π, on the other hand, is largest for systems where electrons are of *indeterminable* speed and is smaller when the system contains more relaxed electrons, i.e., low momentum.

Shannon entropies have been used as measures of basis set quality [3–6], and have been related to various properties such as ionization potentials [7] and geometrical parameters [8]. Recently, a similarity index based on Shannon entropy was introduced, together with the concept of local entropy based on the partitioning of the charge density over the basins of atoms and functional groups [9]. Furthermore, it was found that Shannon entropies in both spaces can serve as useful tools in interpreting the wave function, in particular, characteristics of different correlated methods [10], and following a reaction path [11]. The Shannon *profiles* in these cases yield insights into the chemistry of the systems that are not apparent from the energy profiles.

We have also reported that the Shannon entropy in position space is accessible experimentally through the mean excitation energy [12]. Aside from lending a physical foundation to S_ρ, the kinetic stopping theory also promises a link between the momentum and position space density through experimental data [13]. In this paper, the behavior of the position and momentum space Shannon entropies is analyzed via the use of simple models which incorporate the asymptotic and cusp constraints. An expression for the position space Shannon entropy occurring in the stopping power formalism is derived from the model density. All values in this paper are in Hartree atomic units.

II. RESULTS AND DISCUSSION

A. Shannon entropies of model densities

We first wish to examine the effects of the asymptotic behavior of the density on the entropies, in particular the Shannon entropy. It is known that an upper bound to the asymptotic behavior of the charge density is [14–17]

$$\rho \propto r^{2\beta} e^{-2(2I_1)^{1/2} r}, \tag{2.1}$$

where I_1 is the first ionization potential of the system and $\beta = [Z - N + 1/(2I_1)^{1/2}] - 1$. For simplicity, let us adopt a model where the charge density behaves as Eq. (2.1) throughout the whole space and not just in the asymptotic regions. We apply a more general asymptotic form of the charge density [18], which does not include the $r^{2\beta}$ prefactor, thereby incorporating a hydrogenic model. We wish to compute unit normalized Shannon entropies by imposing the corresponding normalization condition on ρ,

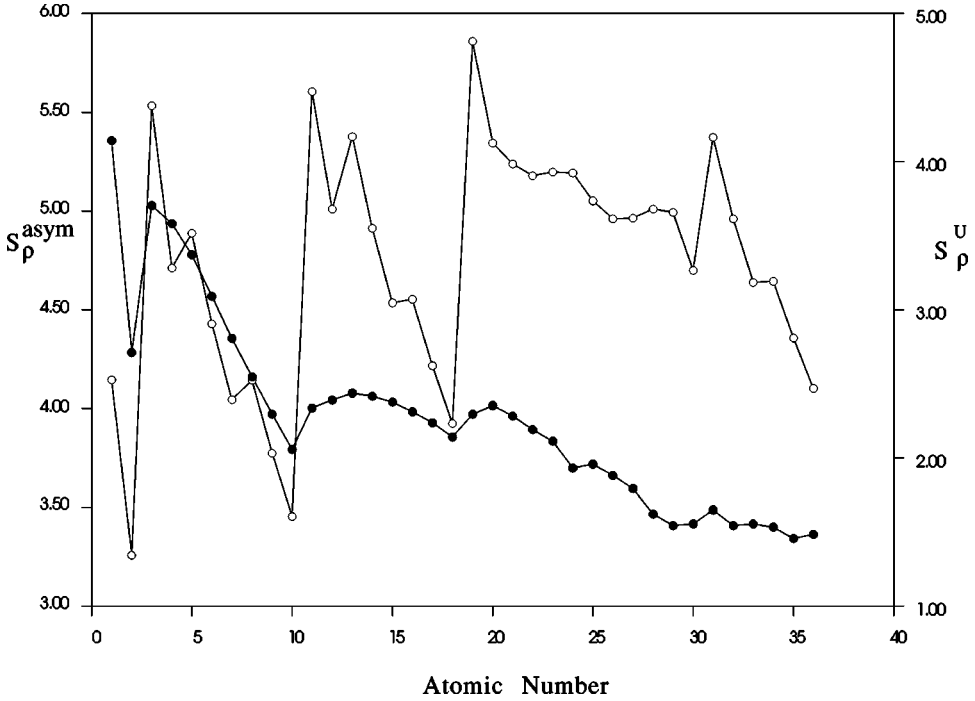

FIG. 1. Unit normalized Shannon entropy (solid circles) and unit normalized asymptotically constrained position space model entropy (open circles) vs atomic number for neutral atoms.

$$\int_0^\infty 4\pi C e^{-2(2I_1)^{1/2}r} r^2 dr = 1. \tag{2.2}$$

The above expression yields a value of $C = 2\sqrt{2} I_1^{3/2}/\pi$ for a unit normalized density.

One may then substitute the form of the charge density in Eq. (2.1) into Eq. (1.1):

$$S_\rho^{asym} = -\int_0^\infty 4\pi C e^{-2(2I_1)^{1/2}r} \ln[Ce^{-2(2I_1)^{1/2}r}] r^2 dr \tag{2.3}$$

to yield the Shannon entropy as

$$S_\rho^{asym} = 3 - \ln\left[\frac{2\sqrt{2} I_1^{3/2}}{\pi}\right]. \tag{2.4}$$

The above equation provides a link between the Shannon entropy of a simple model charge density and the ionization potential of a system. The relationship has physical sense within this context because a higher ionization potential implies that the electron-nuclear forces are larger and there is less electronic shielding (i.e., less electronic repulsions) which implies a situation of a more localized charge density and hence a lower entropy. We note that a higher value of I_1 (for atoms with $I_1 <$ unity which is obeyed for all atoms) would yield a lower value of S_ρ^{asym}. Conversely, a lower ionization potential would imply lesser electron-nuclear forces, more electronic repulsions hence a larger entropy as is indicated by the above equation.

We have plotted in Fig. 1 the value of this asymptotic model Shannon entropy using the inonization potentials reported in Ref. [19] as a function of atomic number along with the real values that were computed directly from Eq. (1.1) using a 6-311G Gaussian type basis set at the CISD (configuration interaction with single and double excitations) level. The features obtained from the Shannon entropies vs atomic number plot using Gaussians are virtually identical to those obtained using Slater-type orbitals [20].

The similarity between the two curves and the ability of the simple model to correctly reproduce the gross features present in the Shannon entropy are remarkable. One observes that the real entropy has a decreasing tendency as a function of Z, i.e., the influence of a higher nuclear charge through the potential $(-Z/r)$ initiates a contraction of the charge density leading to a lower entropy. For the model density, the gross features (peaks, valleys) are the same as the correct one, however the values are different and the decreasing tendency is not present. This is due to the fact that the cusp is not modeled correctly, resulting in lesser contraction of the density in the core region leading to a larger entropy. Correct modeling of the cusp requires that the logarithmic derivative of the spherically averaged density at the nucleus satisfies Kato's condition [21]

$$\rho'(0) = -2Z\rho(0). \tag{2.5}$$

For all the cases studied, Z is larger than $(2I_1)^{1/2}$, thus the exponent of the exponential would be smaller than that required by the cusp condition, therefore the functional form would be more slowly decaying than that required by the cusp condition. Upon substitution in Eq. (2.3), a more slowly decaying exponential would result in a larger value of the integral, hence larger entropy, which explains the nondecreasing tendency (as a whole) of the model entropy. Note also that the model density correctly reproduces the positions of the local minima in the Shannon entropy, which occur at the noble gases, and correspond to localized distributions.

The relationship between entropy and ionization potential should not be surprising as we obtained an empirical relationship between ionization potentials and the differences in

densities as measured from an entropy perspective [7]. Furthermore, these results reinforce the idea that the Shannon entropy is a measure of the electron correlation in a system since the simple model used is exact in the asymptotic regions, precisely where one would expect that relative electron correlation[1] effects would be greatest, i.e., with a correct modeling of the asymptotic regions we are able to reproduce the gross features in the Shannon entropy of atoms. It is also interesting to note that establishing a relationship between the ionization potential and entropies would allow one to establish approximate relationships between the entropy and other chemical reactivity parameters such as hardness or its inverse, softness, which emanate from density-functional formalisms. In the finite difference approximation, the hardness, η is [18]

$$\eta = \frac{I_1 - A}{2}, \tag{2.6}$$

where A is the electron affinity of the system. Keeping A fixed, a higher hardness would mean a higher I_1, i.e., it is more difficult to remove the outermost electron. From Eq. (2.4), this would result from a lower entropy—a more localized density—indicating a tendency of the system to ''hold on'' to this electron. On the other hand, a large entropy (more delocalized system) would emanate from a smaller I_1 leading to a lower hardness of the system. Thus, there is a physical validity to these approximate relationships.

Note that in the model presented, only the asymptotic (large r) behavior of the density is correctly modeled since the cusp condition is not treated explicitly here. Adding the cusp constraint in the model would result in its satisfaction for only those atoms where $Z=(2I_1)^{1/2}$. Imposing the cusp condition through the exponential parameter and relaxing the asymptotic behavior,

$$\rho \propto e^{-2Zr} \tag{2.7}$$

yields a model entropy

$$S_\rho^{cusp} = 3 - \ln[Z^3/\pi]. \tag{2.8}$$

The similarity in behavior is remarkable between this model entropy as a function of Z presented in Fig. 2 and that of the true entropies of the beryllium atom isoelectronic sequence, which were computed from accurate configuration interaction wave functions.

From the above equation, one would expect that a plot of S_ρ^{cusp} vs $\ln Z$ for an isoelectronic series should be linear with a slope of -3 and an intercept of 4.14. Fits of our data, which were computed from accurate configuration interaction wave functions, yielded slopes of -4.65 for the Ne isoelectronic series and -3.80 for the Be series, while the intercepts were found to be 11.87 and 8.76, respectively, with both curves having correlation coefficients greater than 0.990. These results provide evidence that the Shannon entropy is sensitive to the cusp effects within this model. Also notable is that while the cusp modeled entropy behaves similarly to the true entropy for isoelectronic series, this is not the case for the entropies of the neutral atoms as a function of atomic number (even though gross trends are similar; see Fig. 1) hence stressing the importance of the asymptotic behavior to the entropy.

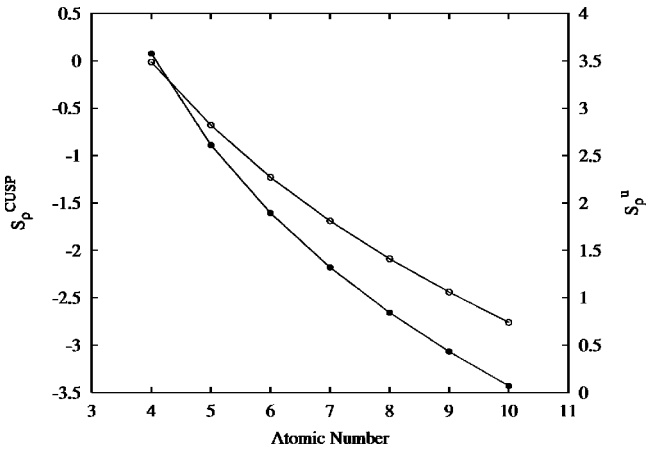

FIG. 2. Position space Shannon entropy for the beryllium isoelectronic sequence (solid circles) and the cusp constrained position space model entropy (open circles) as a function of atomic number.

It is known that the momentum density behaves asymptotically with a leading term of p^{-8}, whose expansion coefficient, B_8, is the derivative of the charge density around the nucleus, thus incorporating the effects of the electron-nuclear cusp condition in the asymptotic behavior of the momentum density [22–24]. Hence a system that exactly obeys the cusp condition will also yield an asymptotically exact momentum density, at least in the leading term. We may find a simple analytical expression for the momentum density by taking the square root of the charge density of the model obeying the asymptotic form of the charge density to obtain a wave function,

$$\psi(r) \propto e^{-(2I_1)^{1/2}r}. \tag{2.9}$$

Setting $\alpha=(2I_1)^{1/2}$, we Fourier transform Eq. (2.9),

$$\tilde{\psi}(p) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty e^{-\alpha r} \frac{\sin(pr)}{pr} r^2 dr = \left(\frac{2}{\pi}\right)^{1/2} \frac{2\alpha}{(\alpha^2+p^2)^2}, \tag{2.10}$$

which yields a unit normalized momentum density of

$$\pi(p) = \frac{8}{\pi^2} \frac{\alpha^5}{(\alpha^2+p^2)^4}. \tag{2.11}$$

[1]The term relative electron correlation is defined here as the percentage difference between the correlated and self-consistent field results (SCF) densities weighted by the former. See, for example, V. H. Smith, Jr., Phys. Scr. **15**, 147 (1977).

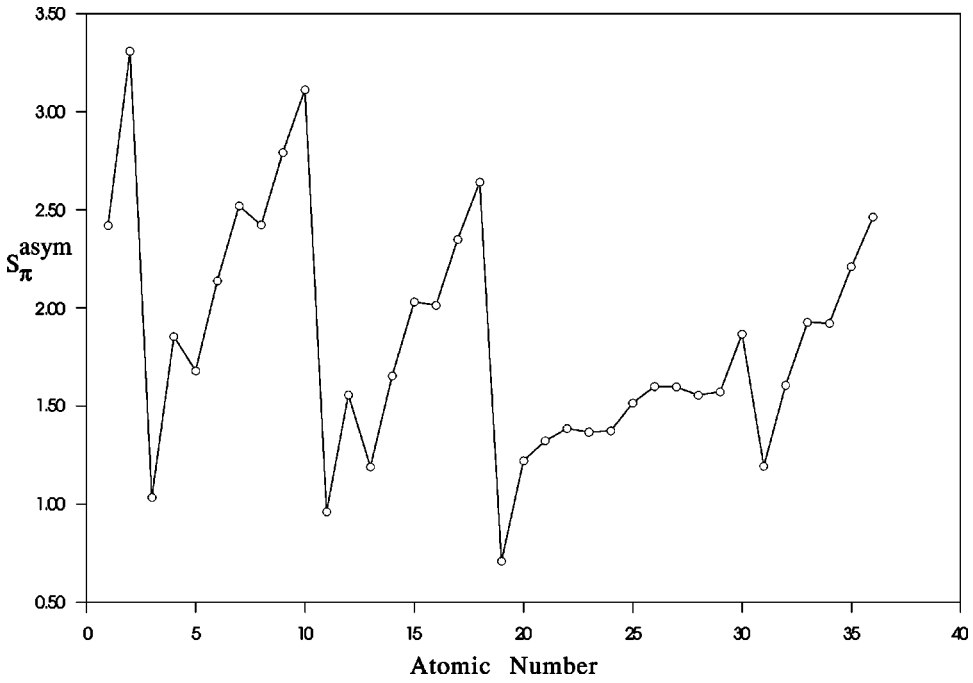

FIG. 3. Unit normalized asymptotically constrained momentum space model entropy vs atomic number for neutral atoms.

Substitution of this form into the momentum space Shannon entropy [Eq. (1.2)] and in a manner analogous to the position space Shannon entropy [Eq. (2.3)], we obtain, using pertinent integral identities,

$$S_\pi^{asym} = -\ln\left[\frac{8\alpha^5}{\pi^2}\right] + 4\left[2\ln 2 - \frac{5}{6} + \ln(\alpha^2)\right]. \quad (2.12)$$

Substituting back for α, we obtain an expression in terms of the ionization potential

$$S_\pi^{asym} = \tfrac{3}{2}\ln I_1 + 2\ln\pi - \tfrac{20}{6} + \tfrac{13}{2}\ln 2. \quad (2.13)$$

One can observe from Eqs. (2.13) and (2.4) that while differing in their constant terms, the momentum space model entropy would display an inverse behavior ($-\frac{3}{2}\ln I_1$) to the position space model entropy ($+\frac{3}{2}\ln I_1$) in accordance with the fact that localization in one space represents delocalization in the other and vice versa. This information is presented in Fig. 3 and on comparing with the position space model entropy (open circles) in Fig. 1 one can observe the inverse behaviors previously stated. On comparing the momentum space model behavior with the true values (Fig. 4) that were computed from the same wave functions as the position space values in Fig. 1, we observe that there is no similarity between the two in contrast to what was presented for the

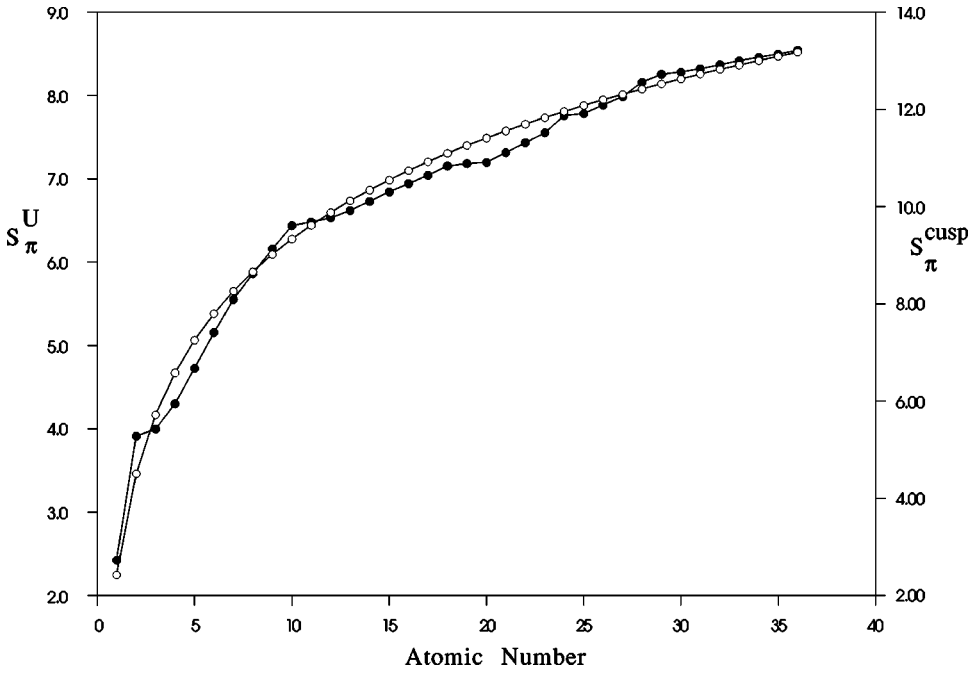

FIG. 4. Unit normalized momentum space Shannon entropy (solid circles) and unit normalized cusp constrained momentum space model entropy (open circles) vs atomic number for neutral atoms.

position space case. While the true S_π is observed to be an increasing function of Z, this is not the case for the model entropy. This result is expected since the asymptotic regions in the position space correspond to the origin in momentum space due to the inverse relationship between the two.

Thus, a reasonable question would be the effect of modeling the position space core correctly in momentum space. We proceed along this avenue by imposing the cusp condition on the model momentum density, which yields that α in the above must be equal to Z, hence the entropy is

$$S_\pi^{cusp} = 3\ln Z + 2\ln\pi + 5\ln 2 - \tfrac{20}{6}. \tag{2.14}$$

Upon analysis of this equation one notes that the behavior would be similar to $3\ln Z$, making this cusp imposed model entropy an increasing function of Z, in agreement with the true entropy. A comparison of the cusp imposed model entropy with the true momentum space entropy is presented in Fig. 4. The similarity between the cusp imposed model and the true entropy should be expected as a correct modeling of the asymptotic regions in momentum space would have to include the cusp condition in the expansion coefficient. One observes that the true entropy has deviations from a logarithmic behavior, which presumably is due to the fact that the true entropy contains not only cusp effects, but also correlation effects.

Furthermore, upon probing the change in the model entropies with respect to the change in nuclear charges, dS/dZ, for the relationships in Eqs. (2.8) and (2.14), one obtains $-(3/Z)$ and $3/Z$ for the position and momentum spaces, respectively. Thus, dS/dZ is inversely proportional to Z in *both* spaces. Hence, we have the result that the functional forms are equivalent in both spaces when one considers the *change* in the entropy and not the entropy itself. Moreover, we see that the values differ in their numerical values by a factor of -1. Based on these results, we expect that a plot of the momentum space model entropy versus the position space one would be linear with a slope of -1. This is an interesting result as we have numerically obtained such a linear relationship for realistic systems under the effects of a solvent field [25].

One could think of generalizing the results above by introducing a simple model similar to what we have proposed where the wave function would be an exponential with a parameter, $-\zeta$, which could be varied to reflect external perturbations realized on the system. In a manner entirely analogous to what we have presented, we could solve for the change in the entropies as a function of the parameter $dS/d\zeta$, to obtain $-3/\zeta$ for position space and $3/\zeta$ for position space, which would yield the linear relationship with slope -1. If one associates uncertainty with entropies, we have the result that the changes in uncertainty with respect to a parameter are linearly related in the position and momentum spaces, within these models used. Summing the two would yield that the sum of the changes in both spaces is zero.

It is also relevant to inquire what would be the sum of the Shannon entropies in both spaces $S_\rho + S_\pi$, for the models presented previously, since an uncertaintylike relationship involving these entropies,

$$S_T = S_\rho + S_\pi \geqslant 3(1+\ln\pi) \tag{2.15}$$

has been shown [3,26] to exist. This entropy sum S_T has been proposed as a *balanced* measure as it takes into account the entropic boundary of the distribution in both spaces. It has been asserted to be a good measure of basis set quality at the atomic [3] and polyatomic levels [5,6]. A study of entropies in both position and momentum space for the water molecule at various correlation levels shows that a balanced density should have a maximal entropy sum. From the entropic point of view, densities which maximize in one space, often do so at the expense of the conjugate space entropy [10].

Summing Eqs. (2.4) and (2.13) yields

$$S_\rho^{asym} + S_\pi^{asym} = 3(1+\ln\pi) + 5\ln 2 - \tfrac{20}{6}. \tag{2.16}$$

Comparing Eqs. (2.15) and (2.16) we note that the bound (2.15) will always be obeyed for the model entropies. Summing the entropies from the cusp constrained model densities in Eq. (2.8) and Eq. (2.14) also yields the result in Eq. (2.16). Interestingly, upon summing Eqs. (2.4) and (2.14) we obtain that in order for the bound to be obeyed,

$$3\left(\ln Z - \frac{\ln I_1}{2}\right) > \frac{20}{6} - \frac{7}{2}\ln(2), \tag{2.17}$$

which is true for all atoms.

B. Model Shannon entropies and stopping power

Recently, we have shown how the Shannon entropy may be experimentally determined within the context of stopping power measurements [12]. The stopping power may be defined as the ability of a material to be penetrated by a charged particle. Now, within this context, the mean excitation energy I, which occurs in the Bethe-Bloch formulation [27] of the stopping power, may be expressed as

$$Z\ln I = \sum_l f_l \ln\hbar\omega_l, \tag{2.18}$$

where the summation is over virtual oscillators of strength f_l and frequency ω_l and Z is the atomic number. As a first approximation, since f_l is closest to one for significant transitions, one may consider $\hbar\omega_s \approx I_s$, where I_s is the ionization potential of the sth electron [28], thus Eq. (2.18) may be rearranged in terms of the mean ionization potential $\overline{I}$ as

$$Z\ln I = Z\ln\overline{I} = \sum_s \ln I_s, \tag{2.19}$$

where the summation is over all electrons. This approximation of equating the mean excitation energy with the mean ionization potential has been shown to be a good one for lighter elements [28].

There is another approximation called the local plasma approximation [29,30], where the mean excitation energy may be expressed in terms of the charge density

$$Z \ln I = \int \rho(\mathbf{r}) \ln[\gamma \hbar \omega_p(\mathbf{r})] d\mathbf{r}, \tag{2.20}$$

where γ is a correction for the shift in the plasma frequency $\omega_p(\mathbf{r})$ due to the chemical environment, and the plasma frequency is defined as

$$\omega_p(\mathbf{r}) = [4\pi e^2 \rho(\mathbf{r})/m]^{1/2}, \tag{2.21}$$

where e and m are the electron charge and rest mass. It has been remarked by Inokuti *et al.* [31] that there might be an analytical derivation to go from the mean excitation energy in terms of oscillator strengths, Eqs. (2.18) to (2.20) in terms of the charge density.

Rearranging Eq. (2.20), and spherically averaging,

$$Z \ln I = \int_0^\infty 4\pi r^2 \rho(r) \ln[\gamma \hbar \omega_p(r)] dr, \tag{2.22}$$

we are led to the expression [12]

$$Z \ln I = \frac{-S_\rho}{2} + \frac{Z \ln 4\pi}{2} + Z \ln \gamma \tag{2.23}$$

yielding the Shannon entropy,

$$S_\rho = Z \ln 4\pi + 2Z \ln \gamma - 2Z \ln I \tag{2.24}$$

or in terms of the mean ionization potential $\overline{I}$,

$$S_\rho = Z \ln 4\pi + 2Z \ln \gamma - 2Z \ln \overline{I}. \tag{2.25}$$

Let us compare this expression for the entropy with the expression obtained from our model density. In the treatment of the Shannon entropy in terms of the mean excitation energy (or mean ionization potential using the approximation), the density is normalized to Z ($Z=N$ for neutral species). Normalizing the model density to Z we obtain $C = 2\sqrt{2} Z I_1^{3/2}/\pi$, which upon substitution into Eq. (2.3) yields an entropy

$$S_\rho^{asym} = Z\left(\ln 4\pi + 3 - \frac{7}{2} \ln 2 \right) - Z \ln Z - \frac{3}{2} Z \ln I_1, \tag{2.26}$$

where the subscript is used to denote the first ionization potential. Upon comparing Eqs. (2.25) and (2.26) the similarities between the two expressions are striking if one considers the approximations involved, namely, the use of a model density and equating the mean excitation energy with the first ionization potential ($I = I_1$) which implies a homogeneous environment, and thus one reverts to the local plasma approximation. The first terms in Eqs. (2.25) and (2.26) differ by a factor of $0.57Z$. The second terms in the equations are equal if one equates γ with $Z^{-1/2}$ while the third terms differ by $(-Z \ln I)/2$. Alternatively, one might think of rewriting Eq. (2.26) as a three term equation similar to Eq. (2.25), yielding

$$S_\rho^{asym} = Z \ln 4\pi + 2Z \ln\left[\frac{e^{3/2}}{2^{7/4}\sqrt{Z}} \right] - \frac{3}{2} Z \ln I_1, \tag{2.27}$$

which may be compared to Eq. (2.24) by equating the argument of the logarithm with γ. It is interesting that the numerical value of the constant in the argument is 1.33 which is close to the $\sqrt{2}$ value of γ that has been proposed [29] and shown by recent numerical calculations [12]. Also, for lighter elements, we see that the logarithmic argument would be approximately one in agreement with the empirical observation that a γ of one should be used in calculations involving light elements [12].

Physically, the similarity between the two relationships [Eqs. (2.25) and (2.26)] is understandable because in stopping power measurements, the incoming charged particle sees and interacts with the asymptotic part of the charge density of the target, and is less affected by what is happening in the core region. Thus, the use of a density with asymptotic constraints is suitable. These two relationships provide evidence of Inokuti's conjecture [31] about a possible analytical relationship between Eqs. (2.18) and (2.20).

The main difference between Eqs. (2.25) and (2.26) lies in the constants (2 and $\frac{3}{2}$, respectively) that precede the $-Z \ln I$ terms. One might speculate that use of a more general asymptotic form such as that in Eq. (2.1) and including the $r^{2\beta}$ prefactor might be what is needed to make the two approaches coincide. This, however is not the case. One finds that the expression for any model density of the form of Eq. (2.1) will yield the factor of $-\frac{3}{2} Z \ln I$ plus additional terms containing I dependencies. Moreover, it may be shown that this factor is a consequence of the particular normalization used.

III. CONCLUSIONS

A model charge density correctly depicting the asymptotic behavior is used to derive an expression for the entropy dependence on the ionization potential, and it is shown how this model entropy possesses the same characteristics as the true entropy. This model provides a connection for the entropy with other chemical reactivity parameters such as hardness and softness. The changes in the position and momentum space entropies as a function of a parameter are shown to be linearly related for these models. We also showed that use of the model density yields an expression for the model entropy that is remarkably similar to the one obtained for the entropy within the local plasma approximation in the stopping power formalism. This result provides evidence of the conjecture that there may be an analytical derivation between the mean excitation energy in terms of oscillator strengths and that in terms of the charge density (the local plasma approximation). It is shown that the momentum space Shannon entropy behavior is largely due to the effects of the cusp region.

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