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Calculating the logarithmic mean excitation energy from the Shannon information entropy of the electronic charge density

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It is shown that within the local plasma approximation, the experimental logarithmic mean excitation energy that occurs in the expression for the stopping power is directly related to the Shannon entropy of the electronic charge density. This energy is calculated from the Shannon entropy of *ab initio* wave functions for several atoms and molecules. The results are consistent with experimental and theoretical values calculated by independent methods. The dependence of the mean excitation energy on the quality of the wave functions is examined. Furthermore, it is shown that the maximum entropy principle can be used as a guide in evaluating the local plasma model. [S1050-2947(98)03706-8]

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I. INTRODUCTION

The ability of a material to be penetrated by charged particles is of wide interest in theoretical physics [1], radiation chemistry [2,3], and biomedicine [4], since it involves many fundamental as well as applied atomic and molecular processes. This ability is conventionally defined as the kinetic energy dE lost by a particle of charge z and velocity v passing through a path length dx. Also known as the stopping power S, it can be calculated according to the Bethe-Bloch equation [1] as

$$S(v,I)=-\frac{dE}{dx}=\frac{4\pi e^4z^2}{mv^2}NZ\left[\ln\frac{2mv^2}{I}-\ln(1-v^2/c^2)\right.$$
$$\left.-v^2/c^2-C/Z-\delta/2\right], \tag{1.1}$$

where e and m are the electron charge and rest mass, N is the number of atoms per unit volume, and Z is the number of electrons for each atom of the target matter. The second and third terms inside the brackets are the relativistic corrections, and c is the speed of light. The last two terms take into account unequal contributions of individual shells and the change of the target density at high energy. The quantity I is the mean excitation energy, which can be experimentally determined from the measured stopping power [5,6]. Conversely, knowledge of I is essential in the theoretical evaluation of the stopping power. The mean excitation energy is of importance since it characterizes how well the target material can absorb energy, independent of the nature and speed of the incident particle. Further aspects of the penetration process, such as the energetic *range* of the projectile, and fluctuations (straggles) in energy, may also be determined based on I. Here, the logarithmic mean excitation energy is defined as the sum of all the logarithmic excitation energies from the ground state $|0\rangle$ to excited states $|n\rangle$ weighted by the dipole oscillator strength f_{0n} of each transition,

$$Z\ln I=\sum_n f_{0n}\ln(E_n-E_0). \tag{1.2}$$

High-quality values of I for hydrogen, obtained using Eq. (1.2), were determined as early as 1930 by Bethe [7]. However, the lack of experimental data for the dipole oscillator strength severely hinders the determination of I in general. Consequently, alternative models were developed, notably among which are the semiempirical method of summations [8,9], and methods using the oscillator strength spectra [10,11] or various moments of the oscillator strength distributions (OSD) [12,13].

In 1953, Lindhard and Scharff [14,15] proposed a statistical model approximating the charge distribution as an averaged homogeneous electron gas and applied this to the evaluation of the logarithmic mean excitation energy. In this *local plasma approximation* (LPA), all individual electronic transitions in Eq. (1.2) are replaced by a collective longitudinal interaction mode. The strength of the photoabsorption frequency due to the collective excitation is further approximated to be the local value of the charge density. It follows that the logarithmic mean excitation energy in Eq. (1.2) may be written as

$$Z\ln I=\int \rho(\mathbf{r})\ln[\gamma\hbar\omega_p(\mathbf{r})]d\mathbf{r}, \tag{1.3}$$

where γ is the correction for the shift in the plasma frequency $\omega_p(\mathbf{r})$ due to the chemical environment of individual particle excitations. The plasma frequency corresponding to a charge density at point $\mathbf{r}$ is

$$\omega_p(\mathbf{r})=[4\pi e^2\rho(\mathbf{r})/m]^{1/2}. \tag{1.4}$$

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Substituting Eq. (1.4) into Eq. (1.3), and making use of the normalization condition of the density, $\int \rho(\mathbf{r})\, d\mathbf{r}=Z$, the logarithmic mean excitation energy (in a.u.) may be expressed in terms of the charge density as

$$2Z\ln I=\int \rho(\mathbf{r})\ln\rho(\mathbf{r})\, d\mathbf{r}+Z\ln 4\pi+2Z\ln\gamma. \quad (1.5)$$

The first term in Eq. (1.5) is the negative of a quantity known as the Shannon information entropy [16], S_ρ, of the electronic charge distribution. Thus, the value of S_ρ can be evaluated directly from the experimental logarithmic mean excitation energy via

$$S_\rho=-2Z\ln I+Z\ln 4\pi+2Z\ln\gamma. \quad (1.6)$$

Correspondingly, the stopping power can be expressed in terms of the Shannon entropy as

$$S[v,\rho(\mathbf{r})]=\frac{4\pi z^2 NZ}{v^2}\left(\frac{S_\rho}{2Z}+\ln[v^2/(\pi^{1/2}\gamma)]-\ln(1-v^2/c^2)-v^2/c^2-C/Z-\delta/2\right). \quad (1.7)$$

The Shannon entropy has recently gained attention due to numerous studies and applications of information theoretical concepts for the analysis of chemical and physical phenomena [17–24]. S_ρ provides a measure of the delocalization of the distribution and has been related to the quality of the basis set [18–22], correlation in the wave function as well as atomic and molecular properties [23,24]. The connection between the Shannon entropy and the first ionization potential energy of atoms within the Koopmans' theorem has been noted by us [23]. It is interesting to note that Eq. (1.6) establishes another connection between the entropy and electronic excitations.

It is also noteworthy that the Shannon entropy of the momentum space density, $S_\pi=-\int \pi(\mathbf{p})\ln\pi(\mathbf{p})d\mathbf{p}$, has been studied extensively by the aforementioned authors [19,21–24]. It has been demonstrated that the momentum space density, particularly from the entropic perspective, provides complementary insight into chemical phenomena of atoms in molecules. The relationship between momentum space density and the stopping power has been advanced by Sigmund [25]. Within this kinetic theory of stopping, a functional relationship between the Compton profile—from which the momentum density can be derived—and the stopping power was developed [26]. Sabin and Oddershede [27] have calculated stopping powers for a variety of systems using both Compton profiles and momentum densities. Since there is no rigorous relationship between $\rho(\mathbf{r})$ and $\pi(\mathbf{p})$ [28], one can see that through the experimental stopping power, Shannon entropy provides a link between the densities in the two spaces. Work investigating this link is currently in progress in this laboratory.

In the present work, we numerically demonstrate that the mean excitation energy of various atoms and molecules can be calculated from the Shannon entropies, most of which were reported earlier by us. Further, we report the mean excitation energies derived from Shannon entropies using different models that include electron correlation and different basis sets to illustrate that previous research done with regard to the maximum entropy principle may be applied to better model the environment of the local plasma approximation. We thus examine the model and basis set effects with regard to delocalized distributions and judge the effects on the mean excitation energy.

II. METHODS AND RESULTS

The Shannon entropies of the first- and second-row atoms were calculated at the Hartree-Fock (HF) level using various basis sets [22]. Near-HF [29] and configuration interaction with single and double excitations (CISD) wave functions of these atoms [23] are also employed. For molecules, we used the wave functions of H_2 and H_2O at the CISD level using the correlation consistent valence triple zeta basis set with polarization functions (cc-pVTZ) [30]. For ethane and acetylene, we used the split-valence 6-31G [31] and the Dunning's double-zeta D95 [32] basis sets, respectively. Finally, for the ammonia molecule, the HF wave function with the 6-31G basis set augmented with double polarization and double diffuse functions [33] was used. The wave functions were obtained employing the GAUSSIAN94 package [34], and all notations are standard therein.

The mean excitation energy was calculated via Eq. (1.6) where γ is set equal to unity. The atomic mean excitation energies derived from the Shannon entropy are tabulated in Tables I and II. We have also reported the theoretical OSD results from the numerical-HF (OSD/numerical-HF) wave functions [35]. We have tested and found that the density of the Near-HF wave functions are very similar to that of the numerical ones. The differences in the densities are in fact less than our integration precision (10^{-5} a.u.). For our practical purpose, it is reasonable to assume that the Shannon entropy calculated from the near-HF wave function is identical to that of the numerical-HF one. In essence, we report here the mean excitation values of the numerical-HF wave functions calculated from both the LPA and the OSD models. It is not our intention to evaluate the merit of the LPA versus other methods (for example, see Refs. [2,36]), but rather to demonstrate the dependence of the mean excitation energy on the quality of the density keeping in perspective established models. To this angle, together with the numerical-HF results, we present the theoretical OSD data from the Hartree-Slater (OSD/HS) wave functions reported by Inokuti and co-workers [12] and the empirical fitting data compiled by Andersen and Ziegler [37] in Fig. 1. From the sparse experimental data listed in Tables I and II, our results show consistently an underestimation of experimental results. However, there is a striking similarity between the

TABLE I. First-row atom mean excitation energies (in eV) calculated from Shannon information entropies, OSD model, and experimental values.

	Level	$I(S_\rho)$	I(OSD/numerical-HF) [35]	Experimental
H	numerical-HF	12.14		14.99 [7]
He	numerical-HF	35.39	39.8	44.3 [12], 41.35 [12]
Li	numerical-HF	26.25	22.06	37.36 [11], 37.4 [12]
	CISD/6-31G	26.72		
	HF/6-31G	26.73		
	HF/3-21G	25.99		
Be	numerical-HF	31.51	30.69	61.7 [12]
	CISD/6-31G	32.50		
	HF/6-31G	32.69		
	HF/3-21G	31.79		
B	numerical-HF	39.30	45.14	
	CISD/6-31G	41.15		
	HF/6-31G	41.12		
	HF/3-21G	40.00		
C	numerical-HF	50.00	62.11	81.3 [12]
	CISD/6-31G	51.26		
	HF/6-31G	51.32		
	HF/3-21G	50.88		
N	numerical-HF	62.88	81.18	78.78 [11], 89.6 [12], 78.0 [12]
	CISD/6-31G	62.68		
	HF/6-31G	63.05		
	HF/3-21G	63.66		
O	numerical-HF	76.22	99.50	93.65 [11], 101 [12], 92.6 [12]
	CISD/6-31G	76.19		
	HF/6-31G	76.84		
	HF/3-21G	77.96		
F	numerical-HF	91.68	119.84	
	CISD/6-31G	92.27		
	HF/6-31G	92.93		
	HF/3-21G	94.17		
Ne	numerical-HF	109.17	142.12	132 [11], 129.5 [12]
	CISD/6-31G	109.60		
	HF/6-31G	110.44		
	HF/3-21G	112.13		

LPA/numerical-HF patterns with the theoretical OSD/HS ones shown in Fig. 1. In addition, numerical deviations would be minimized if the suggested value of $1 \leqslant \gamma \leqslant \sqrt{2}$ was employed. In general, our LPA/numerical-HF values appear to agree slightly better with the empirically fitted data than those from the OSD/numerical-HF wave functions. Their values differ mainly in elements with unsaturated valence orbitals.

For molecular systems, the LPA/numerical-HF values in Table III agree well with the results of Ford and Browne [38], and Meath and co-workers [11,39–43] who employed both experimental data and a theoretical OSD model. For H_2, NH_3, C_2H_4, and C_2H_6, the calculated values of I demonstrate excellent agreement with experimental data, yielding deviations of less than 1%. For CO, HF, HCl, and H_2O, the LPA underestimates I with an average of 12%. The high electronegativities of O, F, and Cl have resulted in highly localized densities, and we conjecture that the homogeneous density model is limited in these instances.

From a statistical perspective, among the distributions satisfying the known constraints of the system, the one with the highest entropy should be selected. This is the maximum entropy principle, proposed by Jaynes [44], which coincides with the requirement of the local plasma model. Recall that a large value of entropy corresponds to a delocalized distribution that yields a better portrayal of the LPA picture. With this in mind, we have chosen different *ab initio* models to gauge the dependency of I on the basis set as well as on the level of theory. Tables I and II show a decrease in the mean excitation energy in going from the HF to the CISD level for all atoms except B and Mg. Equation (1.6) shows an exponential relationship between I and S_ρ,

$$I = 2\sqrt{\pi}\gamma \exp[-S_\rho/2Z]. \tag{2.1}$$

From this, it is apparent that inclusion of electron correlation (which is essentially a delocalization effect of the density) will lead to a higher entropy and therefore a decrease in the mean excitation energy.

TABLE II. Second-row atom mean excitation energies (in eV) calculated from Shannon information entropies, OSD model, and experimental values.

	Level	$I(S_\rho)$	I(OSD/numerical-HF) [35]	Experimental
Na	numerical-HF	99.78	89.67	
	CISD/6-31G	99.45		
	HF/6-31G	99.53		
	HF/3-21G	99.77		
Mg	numerical-HF	100.88	88.51	
	CISD/6-31G	101.27		
	HF/6-31G	101.02		
	HF/3-21G	101.00		
Al	numerical-HF	102.39	96.75	163 [12], 167 [12]
	CISD/6-31G	103.00		
	HF/6-31G	103.18		
	HF/3-21G	103.20		
Si	numerical-HF	107.68	109.52	173 [12]
	CISD/6-31G	107.87		
	HF/6-31G	108.32		
	HF/3-21G	108.24		
P	numerical-HF	114.85	123.92	
	CISD/6-31G	114.74		
	HF/6-31G	115.03		
	HF/3-21G	114.88		
S	numerical-HF	122.22	136.71	
	CISD/6-31G	122.33		
	HF/6-31G	122.63		
	HF/3-21G	122.43		
Cl	numerical-HF	130.96	151.16	176 [12]
	CISD/6-31G	131.03		
	HF/6-31G	131.37		
	HF/3-21G	131.06		
Ar	numerical-HF	140.82	166.88	182 [12], 189 [12]

As for basis set dependency, the behavior of I is more complicated. There is an increase in I going from the 3-21G basis set to the 6-31G basis set for Li, Be, B, and C, but a reverse trend is observed for the remainder of the series. A Shannon study of first- and second-row atoms and diatomics [22] suggests that this is a combined effect of the increasing ability of Gaussian functions to model the density in both the nuclear and valence regions. In the nuclear region, addition of the Gaussian primitives helps to describe the nuclear cusp of the density—a localization effect. On the other hand, in the valence region, functions are augmented to compensate for the faster than exponential decay of the Gaussian primitives—a delocalization effect. The combined conse-

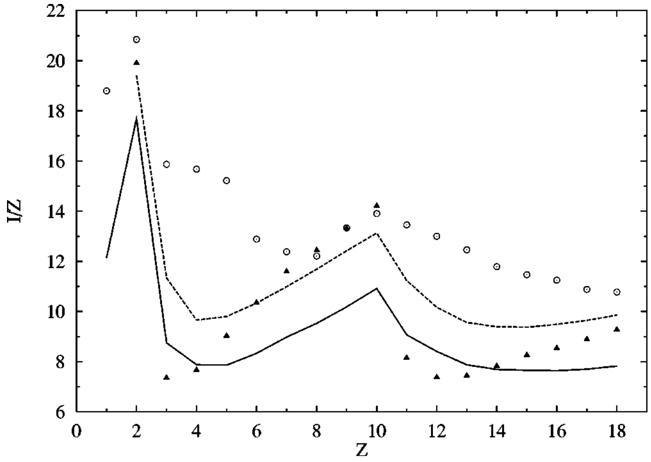

FIG. 1. Mean excitation energies (in eV) per atomic electron I/Z for all atoms through argon. The solid line corresponds to the LPA/numerical-HF results; triangles to OSD/numerical-HF; dashed line to OSD/HS; and circles to empirically fitted data.

TABLE III. Mean excitation energies (in eV) calculated from Shannon information entropies and experimental values for molecules.

	Level	$I(S_\rho)$	Experimental
H_2	CISD/cc-pVTZ	19.19	19.26 [11]
CO	CISD/6-31G	71.71	81.22 [43], 81.36 [38]
HF	CISD/6-31G	85.02	97.03 [41]
HCl	CISD/6-31G	120.45	145.60 [41]
H_2O	CISD/cc-pVTZ	66.45	71.62 [11]
NH_3	HF/6-31++G**	54.34	53.69 [11], 54.59 [42]
C_2H_6	CISD/6-31G	45.66	45.4 [39]
C_2H_4	CISD/D95	48.46	49.92 [40]

quence, measured by S_ρ, shows that in the cases of nitrogen to neon atoms, in which the valence region is most strongly occupied, the effect of increasing the number of Gaussian functions for the valence orbitals overcomes that on the core orbitals. A resulting delocalization in the density leads to a decrease in the mean excitation energy. The same pattern is observed for second-row atoms. Since these atoms have a more diffuse distribution compared to those of the first row, one finds that the effect of the basis set is less pronounced as seen in the cases of Mg and Al.

Lindhard and Scharff [14] introduced γ into the LPA to compensate for the effective frequency $\omega_p(\mathbf{r})$ assumption. Based on the Thomas-Fermi and Hartree distributions, they suggested a value of unity for species in which polarization is not significant and $\sqrt{2}$ for heavier atoms. The use of the wave function in place of the Thomas-Fermi distribution has been encouraged due to the inclusion of the shell structure, which leads to a correct asymptotic behavior of I at high Z [45]. These facts further link γ with the degree of deformation in the charge density. Here, the Shannon entropy may provide an alternative explanation. From Eq. (1.5), if one considers $2Z\ln\gamma$ as a perturbation of the value of the entropy, then a non zero value of $1\leq\gamma\leq\sqrt{2}$ implies a lower information entropy, or a more localized distribution for the system. This is to compensate for the rough assumption of the homogeneous density. An alternative improvement to the LPA is to treat the contribution of each orbital individually [46] or to have separate treatments for the core and valence orbitals [47,48].

We wish to further comment on the accuracy of I calculations based on S_ρ. The agreement between $I(S_\rho)$ reported here and the literature values from different sources should be considered with caution. These wave functions are inexact due to the basis set truncation error plus incomplete (or lack of) treatment of electron correlation and relativistic effects. The availability of exact wave functions will obviously shift the values of I. Since I enters Eq. (1.1) in a logarithmic form, this deviation will be intensified for the value of the stopping power. Results from Tables I and II show that the effect of the basis set on values of I is small. The effect is also expected to be minute for the electron correlation and relativistic corrections since the HF wave functions should have already accounted for more than 99% of the total energy [49]. The deviation in the charge density is further estimated to be of similar magnitude. This is indeed the case, as is apparent in Tables I and II, where the changes in I are small upon the addition of electron correlation.

Finally, there are instances in which the referenced values of I seem to be closer to the HF results than those at the CISD level. The same is also observed, to a lesser extent, for the basis set study, where a larger basis set sometimes produces a larger deviation from the literature values. In these cases, the maximum entropy principle should be used to gauge how well the LPA is being modeled and hence, a lower value of I would be chosen. Note that in cases where the LPA model fails to reproduce accurate results, that is, where the homogeneity approximation does not hold, this principle would intensify the error. Fortunately, reviews of the local plasma model have shown its ''remarkably realistic'' ability in estimating the mean excitation energy [36] and further attributed this ability to the fact that the major contributions to the spectrum of the oscillator strength are those at intermediate energy range. The charge density of the system, then, should strive to fulfill this constraint and at the same time should correctly describe chemical properties of interest. The maximum entropy principle, an independent way of gauging the quality of the basis set and the wave function, offers such a guide.

III. CONCLUSIONS

We have provided a physical foundation for the Shannon entropy by showing that it can be derived from the experimental mean excitation energy within the local plasma approximation. The mean excitation energies of a series of atoms and molecules were computed from the Shannon entropy and show good agreement with experimental values and especially with those from theoretical and semiempirical models. The maximum entropy principle can be used to ensure that the density imitates the LPA well and thus can be used as a constraint in evaluating the LPA model. Furthermore, a direct relationship between the densities in position and momentum space is implied through the entropic connection.

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