Information entropy and Thomas-Fermi theory

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Informational entropies $S_\rho = -\int \rho \ln\rho \, d\vec{r}$ and $S_\gamma = -\int \gamma \ln\gamma \, d\vec{p}$ have been computed from neutral-atom Thomas-Fermi coordinate-space density ρ and momentum density γ. These entropies turn out to be $S_\rho \simeq N(5.59 - 2\ln N)$ and $S_\gamma \simeq N(1.06 + \ln N)$ leading to $S_\rho + S_\gamma \simeq N(6.65 - \ln N)$, strikingly similar in form to the rigorous bound $S_\rho + S_\gamma \geq 3N(1+\ln\pi) - 2N\ln N$ due to Białynicki-Birula and Mycielski. It is conjectured that the informational entropies for atoms may be well represented by $S \simeq N(\alpha + \beta \ln N)$, α and β being universal constants.

Information-theoretic concepts have been employed[1,2] in recent years for synthesis and analysis of electron densities[1] and electron momentum densities[2] of atoms and molecules. Many measures of information-theoretical entropy of a continuous probability distribution have been proposed, the most widely used one being the Shannon entropy. The Shannon entropy for an absolutely continuous distribution with a probability density $p(x)$ on $[a,b]$ is defined as

$$S = -\int_a^b p(x) \ln p(x) dx \quad . \tag{1}$$

An interesting uncertainty relation for informational entropy in quantum mechanics has been obtained by Białynicki-Birula and Mycielski.[3] For wave functions normalized to unity

$$-\langle \ln|\psi(\vec{r})|^2\rangle - \langle \ln|\tilde{\psi}(\vec{p})|^2\rangle \geq (1+\ln\pi)n \quad . \tag{2}$$

Here, $\psi(\vec{r})$ and $\tilde{\psi}(\vec{p})$ are the wave functions in n-dimensional position and momentum spaces, respectively.

On simplification Eq. (2) leads to

$$S_\rho(N) + S_\gamma(N) \geq 3N(1+\ln\pi) - 2N\ln N$$
$$= N(6.43 - 2\ln N) \quad . \tag{3}$$

Here, $S_\rho(N)$ and $S_\gamma(N)$ are information entropies in coordinate and momentum spaces:

$$S_\rho(N) = -\int \rho(\vec{r}) \ln\rho(\vec{r}) d\vec{r} \tag{4a}$$

and

$$S_\gamma(N) = -\int \gamma(\vec{p}) \ln\gamma(\vec{p}) d\vec{p} \quad . \tag{4b}$$

The densities $\rho(\vec{r})$ and $\gamma(\vec{p})$ in (4a) and (4b) are normalized to the number of electrons, N, in the system. Białynicki-Birula and Mycielcki describe this inequality as a new, stronger version of the Heisenberg uncertainty relation. The physical meaning of (3) is transparent: the more concentrated the wave function is in coordinate space and the lower the uncertainty in localizing a particle, the lower is S_ρ. However, the corresponding uncertainty in momentum space is high, due to γ being a more diffuse distribution. Thus, $S_\rho + S_\gamma$ *cannot* be decreased *below* a limit—as given by (3). The bound (3) is attained by Gaussian wave functions.[3]

The bound (3) is interesting from another point of view: it stresses the fundamental role played by the electron densities $\rho(\vec{r})$ and $\gamma(\vec{p})$. The treatment of density as a basic variable forms the basis of the density functional formalism.[4] The first approximate density functional model, viz., the Thomas-Fermi (TF) theory, dates as early as 1927. TF theory[5] leads to the correct atomic energies in the limit $Z \to \infty$ and is also capable of yielding quick yet fairly good estimates of atomic expectation values. Another attractive feature of the TF theory is that the solution $\phi(x)$ of the TF equation is universal for neutral atoms. Thus, the TF theory forms a natural starting point in a systematic study of informational entropies for atoms and molecules.

The informational entropy $S_\rho(N)$ is given by (4a). For neutral atoms, within TF theory

$$\rho(r) \frac{2^5 N^2}{9\pi^3} \frac{\phi^{3/2}(x)}{x^{3/2}} = K \frac{\phi^{3/2}}{x^{3/2}} \quad . \tag{5}$$

Here, $\phi(x)$ is the universal TF function, N ($=Z$, the nuclear charge) the number of electrons, and $x = r/b$ the scaled distance, where

$$b = \frac{3^{2/3}\pi^{2/3}}{2^{7/3}Z^{1/3}} = \frac{0.885\,341\,38}{Z^{1/3}} \quad . \tag{6}$$

On evaluation of integrals one finds

$$S_\rho(N) = -N \int \phi^{3/2}\sqrt{x}\,(\ln K + \tfrac{3}{2}\ln\phi - \tfrac{3}{2}\ln x) dx$$
$$\simeq N(5.59 - 2\ln N) \quad . \tag{7}$$

The corresponding entropy in the momentum space, viz., $S_\gamma(N)$ can be evaluated by the procedure[6] of Coulson and March, recently used in a convenient form by Gadre and Matcha.[7] The final expression for $S_\gamma(N)$ is

$$S_\gamma(N) = N\ln(3\pi^2) - N + 3\int \rho(\vec{r}) \ln r \, d\vec{r}$$
$$= N\left[\ln(3\pi^2) - 3\ln b - 1 - 2\int \phi^{3/2} \ln(x)\sqrt{x}\,dx\right]$$
$$\simeq N(1.06 + \ln N) \quad . \tag{8}$$

Combining (7) and (8), the TF theory for neutral atoms yields

$$S_\rho(N) + S_\gamma(N) \simeq 6.65N - N\ln N \quad . \tag{9}$$

This result is strikingly similar to the universal bound (3) of Białynicki-Birula and Mycielski. However, (9) is asymptotically correct, whereas the bound (3) becomes weak in that limit.

The present study brings out an interesting feature of informational entropies, S_ρ and S_γ: the TF theory as well as the bound (3) leads to entropies which incorporate N and $N \ln N$ linearly. One may conjecture that the information entropies S_ρ and S_γ extracted from excellent quality wave functions for atoms and, perhaps, molecules can be represented as

$$S = \alpha N + \beta N \ln N \ , \tag{10}$$

where α and β are more or less universal constants.

The calculations of S_ρ and S_γ from good quality (such as Hartree-Fock) wave functions involve large computational efforts and are currently being undertaken. Our preliminary results on a few atoms seem to vindicate the conjecture (10).

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