Statistical theory of spectra: Statistical moments as descriptors in the theory of molecular similarity

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Abstract

Statistical moments of the intensity distributions are used as molecular descriptors. They are used as a basis for defining similarity distances between two model spectra. Parameters which carry the information derived from the comparison of shapes of the spectra and are related to the number of properties taken into account, are defined.

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I. INTRODUCTION

The basic values in statistical theory of spectra are moments of the intensity distribution $I(E)$. In the case of discrete spectra the $n$–th statistical moment is defined as:

$$M_n = \frac{\sum_{i=1}^{\text{max}} I_i(E) E_i^n}{\sum_{i=1}^{\text{max}} I_i(E)},$$

(1)

where $I_i$ is the intensity of the $i$–th line and $E_i$ is the corresponding energy difference. If the spectral lines are sufficiently close to each other then the spectrum may be approximated by a continuous function. Then the $n$–th moment of the intensity distribution is defined as:

$$M_n = \frac{\int_{C(E)} I(E) E^n dE}{\int_{C(E)} I(E) dE},$$

(2)

where $C(E)$ is the range of the energy for which the integrand does not vanish. It is convenient to consider normalized spectra $I(E) = N I(E)$, where $N = \left( \int_{C(E)} I(E) dE \right)^{-1}$, for which the area below the distribution function is equal to 1. Then

$$M_n = \int_{C(E)} I(E) E^n dE.$$  

(3)

Convenient characteristics of the distributions may be derived from the properly scaled distribution moments. Moments normalized to the mean value equal to zero ($M'_1 = 0$) are referred to as the centered moments. The $n$–th centered moment reads:

$$M'_n = \int_{C(E)} I(E)(E - M_1)^n dE.$$  

(4)

The moments, for which additionally the variance is equal to 1 ($M''_2 = 1$) are defined as

$$M''_n = \int_{C'(E)} I(E) \left[ \frac{(E - M_1)}{\sqrt{M_2 - M_1^2}} \right]^n dE.$$  

(5)

In this work the model spectra are approximated by continuous functions taken as linear combinations of $\text{max}$ unnormalized Gaussian distributions centered at $\epsilon_i$ with dispersions
σ, defined by the parameters $c_i = 1/2\sigma_i^2$, $i = 1, 2, \ldots\ max$:

$$I(E) = N \sum_{i=1}^{\text{max}} a_i \exp \left[ -c_i (E - \epsilon_i)^2 \right]. \quad (6)$$

The normalization constant $N$ is determined so that the zeroth moment of the distribution $I(E)$ is equal to 1.

The $n$-th moment of the distribution is equal to:

$$M_n = N \sum_{i=1}^{\text{max}} \int_{C(E)} a_i \exp \left[ -c_i (E - \epsilon_i)^2 \right] E^n dE. \quad (7)$$

After some algebra we get the expressions for the moments as functions of the parameters describing the height ($a_i$), the width ($c_i$) and the locations of the maxima ($\epsilon_i$). In particular,

$$M_1 = N \sum_{i=1}^{\text{max}} \epsilon_i a_i \sqrt{\frac{\pi}{c_i}}, \quad (8)$$

$$M_2 = N \sum_{i=1}^{\text{max}} a_i \sqrt{\frac{\pi}{c_i}} \left( \frac{1}{2c_i} + \epsilon_i^2 \right), \quad (9)$$

$$M_3 = N \sum_{i=1}^{\text{max}} a_i \epsilon_i \sqrt{\frac{\pi}{c_i}} \left( \frac{3}{2c_i} + \epsilon_i^2 \right), \quad (10)$$

$$N = \left( \sum_{i=1}^{\text{max}} a_i \sqrt{\frac{\pi}{c_i}} \right)^{-1}. \quad (11)$$

According to the so called principle of moments \[1, 2, 3\] we expect that if we identify the lower moments of two distributions, we bring these distributions to approximate identity. In this paper we apply this principle to the theory of molecular similarity. We assume that molecules have similar properties if their intensity distributions and, consequently the corresponding moments, are approximately the same.

We propose that statistical moments of the intensity distributions can be treated as a new kind of molecular descriptors. A very clear meaning has the first moment, $M_1$, which describes the mean value of the distribution. In a similar sense a colour index has been introduced in astronomy \[4\] - its value allows us to compare spectra of different stars (it carries an information about molecules forming the star). The second centered moment, $M'_2$, is the variance which gives the width of the distribution. $M''_3$ is the skewness coefficient which describes the asymmetry of the spectrum. The kurtosis coefficient $M''_4$ is connected to the excess of the distribution.
II. THEORY AND THE MODEL SPECTRA

According to the method of moments, the shapes of two distributions are more similar if the number of identical moments is larger. Similarity of distributions in two- and three-moment approximations, in the context of the construction of envelopes of electronic bands, has been analyzed in Refs. [5, 6, 7, 8]. Analogously, we define similarity parameters $S_{i_1i_2...i_k}^k$ ($k$ is the number of properties taken into account in the process of comparison) as a normalized information derived from a comparison of two distributions, referred to as $\alpha$ and $\beta$:

$$S_{i_1}^1 = \sqrt{D_{i_1}^2},$$

$$S_{i_1i_2}^2 = \sqrt{\frac{1}{2} (D_{i_1}^2 + D_{i_2}^2)}, \quad i_1 < i_2$$

$$S_{i_1i_2...i_k}^k = \sqrt{\frac{1}{k} (D_{i_1}^2 + D_{i_2}^2 + \ldots + D_{i_k}^2)}, \quad i_1 < i_2 < \ldots < i_k$$

$$S_{n_112...i_n}^n = \sqrt{\frac{1}{n} \sum_{i=1}^{n} D_i^2}. $$

Here $n$ is the total number of properties taken into account in the comparison of the two spectra and $i_k = 1, 2, \ldots n$ ($k = 1, 2, \ldots n$), correspond to a specific property. In particular, as the property number one ($i_k = 1$) we take the first moment, as the property number two ($i_k = 2$) we take the second centered moment, number three ($i_k = 3$) - the asymmetry coefficient, number four ($i_k = 4$) - the kurtosis coefficient. In this paper we take $n = 4$ and the corresponding similarity distances are defined as follows:

$$D_1 = 1 - \exp \left[ - \left( M_1^\alpha - M_1^\beta \right)^2 \right],$$

$$D_2 = 1 - \exp \left[ - \left( M_2^\alpha - M_2^\beta \right)^2 \right],$$

$$D_3 = 1 - \exp \left[ - \left( M_3^\alpha - M_3^\beta \right)^2 \right],$$

$$D_4 = 1 - \exp \left[ - \left( M_4^\alpha - M_4^\beta \right)^2 \right].$$

The values of all the descriptors may vary from 0 (identical properties) to 1.
We also define an additional parameter which may be evaluated if both spectra we are going to compare are available:

\[ D = \frac{1}{2} \int_{C(E)} |I'^\alpha(E) - I'^\beta(E)|dE. \]  

(20)

This parameter is given by the integral of the module of the difference between the compared distributions and is not related to the moments. In the definition of \( D \), \( I' \) denotes the distributions transformed so that their averages are the same. If we compare two distributions of the same shape then \( D = 0 \). If two distributions do not overlap at all, then \( D = 1 \). It is important to note that the distribution moments are defined as numbers attached to a given spectrum and the similarity distances \( D_n \) are easily derived from the knowledge of these numbers. The parameter \( D \), though it gives accurate information about similarity of two spectra, is rather cumbersome since it may be derived only if the complete spectra are given.

If two model molecules (or rather their spectra) are identical, up to the accuracy determined by the considered properties, then all \( S_{i_1 i_2 \ldots i_k} \) are equal to 0. The maximum value of \( S_{i_1 i_2 \ldots i_k} \) is 1 and corresponds to two spectra with no common features within the considered set of properties.

The result of a comparison of two different objects depends not only on the number of properties taken into account but also on their choice (\( i_1 \) or \( i_2 \) or \( \ldots \) \( i_n \)). Therefore the quantities \( S_{i_1 i_2 \ldots i_k} \) defined in Eq. (12) - (15) should be averaged by taking all combinations of the indices \( i_k \). Thus, we define parameters \( S_k \) as the appropriate averages of \( S_{i_1 i_2 \ldots i_k} \):

\[ S_k = \left( \frac{n}{k} \right)^{-1} \sum_{i_1 < i_2 < \ldots < i_k} S_{i_1 i_2 \ldots i_k}. \]  

(21)

In particular, in our case:

\[ S_1 = \frac{1}{4} \sum_{i_1=1}^{4} S_{i_1}^{i_1}, \]  

(22)

\[ S_2 = \frac{1}{6} \sum_{i_1 < i_2}^{4} S_{i_1 i_2}^{i_1 i_2}, \]  

(23)

\[ S_3 = \frac{1}{4} \sum_{i_1 < i_2 < i_3}^{4} S_{i_1 i_2 i_3}^{i_1 i_2 i_3}, \]  

(24)

\[ S_4 = S_{i_1 i_2 i_3 i_4}^{i_1 i_2 i_3 i_4}. \]  

(25)
FIG. 1: Two intensity distributions (solid and dashed lines) and the corresponding similarity parameters $S_4$ (sequence I).

III. RESULTS AND DISCUSSION

In order to illustrate our approach, we took model spectra consisting of two bands, i.e. having two maxima ($\text{max} = 2$):

$$\Gamma'(E) = N \left[ a_1 \exp \left[ -c_1(E - \epsilon_1)^2 \right] + a_2 \exp \left[ -c_2(E - \epsilon_2)^2 \right] \right],$$  \hspace{1cm} (26)

where $\gamma = \{c_1, a_1, \epsilon_1, c_2, a_2, \epsilon_2\}$. In order to see relations between molecular spectra, defined in Eq. (26) and the similarity indices defined in Eqs. (16) - (20) and (22) - (25) in a simple and transparent way, we study three sequences of spectra, where in each sequence only one parameter has been modified: $c_2$ in sequence I, $a_2$ in sequence II, $\epsilon_2$ in sequence III.

(a) Sequence I corresponds to the situation when a symmetric spectrum consisting of two identical Gaussian distributions shifted relative to each other by $\epsilon_2 - \epsilon_1 = 1$ ($a_1 = a_2 = 1.0, \epsilon_1 = 1.2, \epsilon_2 = 2.2, c_1 = c_2 = 5.0$) transforms to a distribution in which the width of one of the Gaussians changes due to the change of the parameter $c_2 = 5.0 + \delta c$,
where $\delta c \in (0; 19.8)$. Then, we compare shapes of intensity distributions $I^\alpha(E)$ and $I^\beta(E)$, where $\alpha = \{5.0, 1.0, 1.2, 5.0, 1.0, 2.2\}$, $\beta = \{5.0, 1.0, 1.2, 5.0 + \delta c, 1.0, 2.2\}$.

In Fig. 1 spectra corresponding to $\delta c = 0$ (solid lines) and $\delta c > 0$ (dashed lines) are compared. In each case values of $\delta c$ and $S_4$ are given. A correlation between these two numbers and between shapes of the spectra is clearly seen. The value of $S_4$ increases when the two spectra become less similar.

(b) Sequence II corresponds to the same symmetric spectrum as before ($a_1 = a_2 = 1.0$, $\epsilon_1 = 1.2$, $\epsilon_2 = 2.2$, $c_1 = c_2 = 5.0$) transforming to the distributions in which the height of one of the Gaussians changes due to the changes of $a_2 = 1.0 + \delta a$, where $\delta a \in (0; 9.9)$. Then, we compare shapes of intensity distributions $I^\alpha(E)$ and $I^\beta(E)$, where $\alpha = \{5.0, 1.0, 1.2, 5.0, 1.0, 2.2\}$, $\beta = \{5.0, 1.0, 1.2, 5.0, 1.0 + \delta a, 2.2\}$.

In Fig. 2 spectra corresponding to $\delta a = 0$ (solid lines) and $\delta a > 0$ (dashed lines) are compared. In each case values of $\delta a$ and $S_4$ are given. The conclusions are similar to...
FIG. 3: Two intensity distributions (solid and dashed lines) and the corresponding similarity parameters $S_4$ (sequence III).

those in the case of Fig. 1.

(c) Sequence III corresponds to a similar situation as before, except that the maxima in $I^\alpha$ are shifted by 1.5 rather than by 1 ($a_1 = a_2 = 1.0$, $\epsilon_1 = 1.2$, $\epsilon_2 = 2.7$, $c_1 = c_2 = 5.0$). $I^\alpha$ transforms to the distribution $I^\beta$ for which one of the gaussian distribution changes the location of the second maximum $\epsilon_2 = 2.7 - \delta \epsilon$, where $\delta \epsilon \in (0; 0.99)$. Then, we compare shapes of intensity distributions $I^\alpha(E)$ and $I^\beta(E)$, where $\alpha = \{5.0, 1.0, 1.2, 5.0, 1.0, 2.7\}$, $\beta = \{5.0, 1.0, 1.2, 5.0, 1.0, 2.7 - \delta \epsilon\}$.

In Fig. 3 spectra corresponding to $\delta \epsilon = 0$ (solid lines) and $\delta \epsilon > 0$ (dashed lines) are compared. In each case values of $\delta \epsilon$ and $S_4$ are given. The conclusions are similar to those in the cases described by Figs. 1 and 2.

The molecular descriptors [statistical moments of $I^\beta(E)$] are plotted in Fig. 4 versus $\delta c$ (sequence I), $\delta a$ (sequence II), $\delta \epsilon$ (sequence III). In case of sequence I, it is clear that the considered change of the spectrum leads to a decrease of the first moment (the intensity is
shifted towards smaller energies). The dispersion of the whole distribution also decreases ($M'_2$). The asymmetry of the spectrum changes from totally symmetric ($M''_3 = 0$) to asymmetric ($M''_3 \neq 0$). The kurtosis coefficient $M''_4$ changes as it is presented, in a non-monotonic way. It is interesting that for $M''_3$ and $M''_4$ minima appear for $\delta c \neq 0$. In the case of sequence II, with an increase of $\delta a$ the first moment is shifted towards higher values and the dispersion of the whole spectrum decreases. The asymmetry of the spectrum decreases and the kurtosis parameter increases. In case of sequence III, shifting the second maximum $\epsilon_2$ to the smaller energies results in a distribution with one maximum instead of two and the intensity is shifted towards smaller energies. In consequence the first moment decreases. The whole distribution becomes more narrow and, consequently, we observe decreasing of $M'_2$. For all $\delta \epsilon$ distributions are symmetric ($M''_3 = 0$) and the kurtosis parameter increases.

Fig. 5 presents $D$ defined in Eqs. (16) - (20). In the case of sequence I, if $\delta c = 0$, we compare two identical distributions and all the descriptors are equal to zero. The most sensitive to the changes of $\delta c$ is in this case $D$, contrary to the other descriptors which are nearly constant. The two distributions are rather similar in sense of the average value, of the width, of the asymmetry and of the kurtosis (the values of $D_1, D_2, D_3, D_4$ are small and the corresponding curves cross). In case of sequence II, we observe small values of $D_2$ and $D_1$, that indicates large similarity of the two distributions in sense of the width and of the average values. For small values of $\delta a$ we observe crossings between $D_3, D_4$ and $D$. The most sensitive to the changes of $\delta a$ is $D_4$. In case of sequence III, the behaviour of $D_1$ and $D_2$ is very similar. Both spectra are totally symmetric ($M''_3^{\alpha} = M''_3^{\beta} = 0$). Therefore $D_3 = 0$ for all $\delta \epsilon$. $D_4$ and $D$ cross and change very substantially contrary to $D_1$ and $D_2$ which are nearly constant.

Fig. 6 presents similarity parameters $S_k$ for $k = 1, 2, 3, 4$ [Eqs. (22) - (25)]. Small values of $S$ correspond to high similarity of the model spectra. In particular, if $\delta c = 0$ (sequence I) then $S_k = 0$ for all $k$. As we can see, $S$ is the smallest for $k = 1$ and increases with increasing $k$. Analogously to the sequence I, $S_1 < S_2 < S_3 < S_4$ for all $\delta a$ (sequence II) and for all $\delta \epsilon$ (sequence III). Intuitively, we expect that two systems which are similar to each other when only one property is considered may exhibit more differences if we look at the systems in more detail, taking into account more properties. These features can be seen in Fig. 6.
FIG. 4: Moments of the distributions as functions of $\delta c$ (sequence I), $\delta a$ (sequence II), $\delta \epsilon$ (sequence III).
IV. CONCLUSIONS

Statistical moments describe in an adequate way the degree of similarity of two-band model spectra. Though the mathematical model describing shapes of the spectra is relatively simple, it reflects the behaviour of real molecular spectra. Three parameters: $c$, $a$ and $\epsilon$, influence different aspects of the shapes of spectra and the resulting values of $D$. In particular, parameters $D$ and corresponding $S$ are the smallest if $a$ and $\epsilon$ are constant (sequence I). In these cases spectra are only slightly modified by $\delta c$ (Fig. 1). Larger differences of spectra are caused by parameter $\delta a$, while $c$ and $\epsilon$ are constant (sequence II). The influence of $\epsilon$ on spectra is also large (sequence III). The additional parameter $D$ introduces some independent information about spectra. Contrary to the case of single-band model spectra studied in our previous paper [9], where its behaviour is very similar to $D_4$, here it appears to be the most sensitive index (sequence I).
Summarizing, we demonstrated that spectral density distribution moments can be used for defining similarity indices of spectra. By grouping molecules according to the spectral density distribution moments we can get a chance to discover new characteristics in the field of molecular similarity and in particular it may be a tool for studies in the area of computational toxicology [10, 11, 12].
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