PHYSICAL REVIEW A VOLUME 40, NUMBER 10 NOVEMBER 15, 1989

Spectral distributions in a model N-electron Hamiltonian

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(Received 24 April 1989)

A study on the energy-level distribution of the Pariser-Parr-Pople Hamiltonian has been performed. In particular, relations between the values of the electron interaction parameters, the symmetry of the core potential, and the form of the secular distribution of the energy-level density have been investigated. The density is shown to be Gaussian in the physically significant range of the parameter values. However, very strong deviations from the Gaussian behavior have been observed at the limit of the very weak electron-core interaction. The secular density distribution functions have been used to predict the Hamiltonian spectra in very good agreement with the results of the matrix diagonalization. Spacings of the nearest-neighbor levels behave mainly in a Poisson-like form, showing the existence of approximate hidden symmetries even in the case of highly nonsymmetric core potentials.

I. INTRODUCTION

Two different, complementary approaches may be used in order to describe the eigenvalue spectrum of an operator. The first approach is aimed at a detailed evaluation of individual eigenvalues and has resulted in developing many approximate methods, in most cases derived from the variation principle or from the perturbation theory. The second approach focuses on properties of the entire spectrum rather than of the individual eigenvalues. The set of eigenvalues is then treated as a statistical ensemble and its properties are derived from a knowledge of the moments of the spectral distribution. Though both approaches originated at approximately the same time, more than half a century ago, most of the work on many-electron operator spectra has been concerned with specific eigenvalues, mainly with the lowest ones. Perhaps the most important early contribution to the statistical properties of many-electron spectra has been by Rosenzweig and Porter in 1960.[1] Work on this subject was rather scarce during the following two decades. One should mention here formal developments by Moszkowski,[2] Layzer,[3] Ginocchio,[4] and empirical studies by Parikh[5] and by Cowan.[6] The statistical spectroscopy of the nuclei developed into a broad field at the same time. The contributions by Ratcliff,[7] French *et al.*,[8] and Nomura,[9] though explicitly concerned with the nuclear structure, contain many results valid for any N-particle system. Further references can be found in the reviews published by Brody *et al.*[10] and by French and Kota.[11]

Due to the recent development of experimental techniques an increasing amount of information about transitions between closely packed energy levels both in atoms and in molecules has become available. The applicability of the statistical description to the interpretation of this kind of result has been demonstrated in the case of atoms by Bauche-Arnoult *et al.*[12] and in the case of molecules by Zimmerman *et al.*[13] Studies on the atomic energy-level distribution by Parikh,[5] Cowan,[6] and by the present authors[14] have demonstrated that the secular density is Gaussian-like. However, a more detailed analysis leads to the conclusion that the hypotheses of a Gaussian distribution is not supported by the χ^2 test, unless all energy levels under consideration correspond to the same total angular-momentum quantum number.[14] If the energy-level density distribution function is passed by the χ^2 test as correctly describing the real spectrum, then rather accurate predictions of the location of individual energy levels can be made using just the distribution function.[7,15] This property of the spectra is certainly worth a detailed exploration. In general, obtaining several first moments of spectral distributions directly from a Hamiltonian is a rather easy task—explicit formulas expressing the moments in terms of the interaction parameters are available for many cases.[4,9,10,16] On the other hand, if the secular distribution is Gaussian, then only the two first moments are needed in order to define this distribution. As a consequence, an analysis of the spectral density distribution function may prove to be the simplest way for obtaining an approximate spectrum of a many-electron system.

In this contribution the relations between the form of the spectral density distribution function and the physical characteristics of the system under consideration will be investigated. In order to simplify the formalism it is assumed that the system of nuclei and electrons is described by the Pariser-Parr-Pople Hamiltonian. Thus, it is assumed that the electrons move in a potential field of a molecular "core" formed by a hydrocarbon chain. The spectrum of this Hamiltonian depends upon the geometry of the chain, upon the values of the parameters determining the interaction with the core, and upon the number of electrons and their spin states. It has been found that, except for the case of a very weak core potential, the density of levels is either Gaussian or nearly Gaussian. Then, only the average energy and dispersion are needed to determine the distribution function and, in consequence, the approximate spectrum.

II. THE MODEL

A. The Hilbert space

The Hamiltonian of the present study is defined in a finite-dimensional, antisymmetric and spin-adapted subspace H_N^A of an N-particle Hilbert space taken as the N-fold tensorial product of a one-electron space spanned by a set of $2K$ orthonormal orbitals and composed of a two-dimensional spin space and a K-dimensional orbital space. The spin adaptation means that the space is spanned by eigenvectors of the total spin operators $\hat{S}^2$ and $\hat{S}_z$ corresponding to a given pair of quantum numbers S and M, respectively. The subspace H_N^A is often referred to as the full configuration-interaction (CI) space.[17,18] The dimension of this space is given by the Weyl-Paldus dimension formula[19]

$$D(N,K,S)=\frac{2S+1}{K+1}\begin{bmatrix}K+1\\ \frac{1}{2}N-S\end{bmatrix}\begin{bmatrix}K+1\\ \frac{1}{2}N+S+1\end{bmatrix} . \tag{1}$$

It is assumed that the set of orbitals $\{\varphi_i\}_{i=1}^K$ forming the basis in the orbital space is orthonormal.

The N-electron basis functions $|\lambda;SM,l\rangle$ in the subspace H_N^A are constructed as spin-adapted antisymmetrized products (SAAP's) of the orbitals.[20] They are orthonormal and, besides being antisymmetric

$$\hat{P}|\lambda;SM,l\rangle=\varepsilon(P)|\lambda;SM,l\rangle , \tag{2}$$

fulfill the following eigenvalue equations:

$$\hat{S}^2|\lambda;SM,l\rangle=S(S+1)|\lambda;SM,l\rangle , \tag{3}$$

$$\hat{S}_z|\lambda;SM,l\rangle=M|\lambda;SM,l\rangle , \tag{4}$$

where P is a permutation operator of the electrons and $\varepsilon(P)=\pm 1$ is its parity, λ is an abbreviation for a set of orbital indices used to construct a given SAAP and l distinguishes independent eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ belonging to the same values of S and M. More explicitly, a SAAP may be expressed in the form[18,20,21]

$$|\lambda;SM,l\rangle=\xi_\lambda\hat{A}(|\lambda\rangle|SM,l\rangle) , \tag{5}$$

where

$$\hat{A}=\frac{1}{N!}\sum_P \varepsilon(P)P \tag{6}$$

is the antisymmetrization operator, ξ_λ is the normalization constant, $|SM,l\rangle$ is a pure-spin function being an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ and $|\lambda\rangle$ is a spin-independent orbital function represented in the coordinate space as a product of N orbitals. In the orbital function s_λ orbitals appear once (*singles*, or singly occupied orbitals) and d_λ twice (*doubles*, or doubly occupied orbitals).[20,21] The numbers of singles and doubles in λ are connected by the obvious relation

$$s_\lambda+2d_\lambda=N . \tag{7}$$

It may be shown that[22]

$$l=1,2,\ldots,f(S,s_\lambda) , \tag{8}$$

where

$$f(S,s_\lambda)=\frac{2S+1}{s_\lambda+1}\begin{bmatrix}s_\lambda+1\\ \frac{1}{2}s_\lambda-s\end{bmatrix} . \tag{9}$$

B. Hamiltonian

The N-electron spin-independent Hamiltonian which contains one- and two-electron terms [$\hat{h}_1(1)$ and $\hat{h}_2(1,2)$, respectively] and is written in the coordinate representation as

$$\hat{H}=\sum_{i=1}^{N}\hat{h}_1(i)+\sum_{\substack{i,j\\ i<j}}^{N}\hat{h}_2(i,j) \tag{10}$$

may be represented in the model space H_N^A as[17,18]

$$\hat{H}=\sum_{k,l=1}^{K}(k|l)E_{kl}+\tfrac{1}{2}\sum_{i,j,k,l}^{K}(ij|kl)(E_{ij}E_{kl}-\delta_{jk}E_{il}) . \tag{11}$$

The integrals $(k|l)$ and $(ij|kl)$ describe interactions in the system and are defined as

$$(k|l)=\langle\varphi_k|\hat{h}_1|\varphi_l\rangle \tag{12}$$

and

$$(ij|kl)=\langle\varphi_i(1)|\langle\varphi_k(2)|\hat{h}_2(1,2)|\varphi_l(2)\rangle|\varphi_j(1)\rangle . \tag{13}$$

The operators

$$E_{kl}=\sum_{i=1}^{N}|\varphi_k(i)\rangle\langle\varphi_l(i)| \tag{14}$$

are referred to as shift operators,[23,24] unitary group generators,[17] or replacement operators.[18]

The model described so far does not contain any approximations except for the assumption that the Hilbert space is finite dimensional and that the Hamiltonian is spin independent. In order to simplify the further considerations it is assumed that the form of $\hat{h}_2(1,2)$ and the orbitals are chosen in such a way that

$$(ij|kl)=(ii|kk)\delta_{ij}\delta_{kl} . \tag{15}$$

This assumption is known as the zero-differential-overlap (ZDO) approximation.[25] It has been shown to be fulfilled with reasonable accuracy for the Coulomb interaction potential if the orbitals are chosen as orthonormal $2p\pi$ orbitals localized at the carbon atoms of an unsaturated hydrocarbon molecule.[26] With this interpretation of the orbitals, a model is obtained known as the Pariser-Parr-Pople (PPP) theory of unsaturated hydrocarbons.[25] The orbital indices refer here to the individual carbon atoms forming the molecule. The PPP Hamiltonian has proved very successful in describing properties of planar organic systems with conjugated double bonds. In this model only the delocalized π electrons are considered explicitly moving in a potential field generated by the nuclei, the $(1s)^2$ core of the carbon atoms and the network of σ bonds. Thus it assumes σ-π separability. The PPP approach is a reasonable compromise between a realistic description and simplicity. Therefore, it is frequently used in various kinds of model studies.[17,27]

The PPP Hamiltonian may be obtained by substituting Eq. (15) into the general expression (11) and by assuming that the interaction integrals are chosen to describe the π-electron system. Thus,

$$\hat{H}_{\mathrm{PPP}}=\sum_{k,l}\beta_{kl}E_{kl}+\frac{1}{2}\sum_{k,l}\gamma_{kl}E_{kk}(E_{ll}-\delta_{kl}) , \qquad (16)$$

where γ_{kl} and β_{kl} are, respectively, the so-called Coulomb and resonance integrals. Their values are empirical parameters chosen to reproduce experimental properties (mainly the electronic spectra) of reference molecules.[28] The value of the empirical parameter corresponding to centers k and l is assumed to depend only on the kind of atoms located at these centers and on the interatomic distance. Many empirical formulas for the parameters are available in the literature.[29]

C. Matrix elements

It can be shown[18] that

$$E_{kk}|\lambda;SM,l\rangle=n_k^\lambda|\lambda;SM,l\rangle ,$$

where $n_k^\lambda=0,1,2$ is the occupation number of the orbital φ_k in the configuration λ. Then, the diagonal elements of the PPP Hamiltonian [Eq. (16)] are

$$\begin{aligned}\langle\lambda;SM,l|\hat{H}_{\mathrm{PPP}}|\lambda;SM,l\rangle &\equiv H_{\Lambda\Lambda}\\ &=\sum_k[\beta_{kk}n_k^\lambda+\gamma_{kk}n_k^\lambda(n_k^\lambda-1)/2]\\ &\quad+\frac{1}{2}\sum_{\substack{k,l\\k\neq l}}\gamma_{kl}n_k^\lambda n_l^\lambda . \qquad (17)\end{aligned}$$

However, in a hydrocarbon molecule with equal bond lengths between carbon atoms, all γ_{kk} integrals are the same and all β_{kk} integrals are the same

$$\gamma_{kk}=\gamma_0,\quad \beta_{kk}=\beta_0 , \qquad (18)$$

and the diagonal matrix elements become

$$H_{\Lambda\Lambda}=N(\beta_0-\gamma_0/2)+\frac{1}{2}\sum_{k,l}n_k^\lambda n_l^\lambda\gamma_{kl} . \qquad (19)$$

The off-diagonal matrix elements of $\hat{H}_{\mathrm{PPP}}$ are either proportional to a resonance integral (if the corresponding configurations differ by one orbital) or vanish (if the configurations differ by two or more orbitals). The number of orbitals by which the configurations λ and μ differ is equal to[30]

$$r_{\lambda\mu}=\frac{1}{2}\sum_{i=1}^{K}|n_i^\lambda-n_i^\mu| . \qquad (20)$$

Then,

$$\langle\lambda;SM,l|\hat{H}_{\mathrm{PPP}}|\mu;SM,m\rangle=\begin{cases}\beta_{pq}\langle\lambda;SM,l|E_{pq}|\mu;SM,m\rangle, & \text{if } r_{\lambda\mu}=n_p^\lambda-n_p^\mu=n_q^\mu-n_q^\lambda=1\\ 0, & \text{if } r_{\lambda\mu}>1 .\end{cases} \qquad (21)$$

Substituting the explicit form of the SAAP's, as given by Eq. (5), it follows after some algebra[18,21] that

$$\begin{aligned}&\langle\lambda;SM,l|E_{pq}|\mu;SM,m\rangle\\ &\qquad=\epsilon 2^{|d_\lambda-d_\mu|/2}\langle SM,l|P|SM,m\rangle , \qquad (22)\end{aligned}$$

where

$$\epsilon=\begin{cases}-1, & \text{if } n_p^\lambda+n_q^\lambda=n_p^\mu+n_q^\mu=3\\ 1, & \text{otherwise}\end{cases} \qquad (23)$$

and where P is the lineup permutation which, acting on the orbital indices of λ, puts them into the maximum coincidence with the orbitals of μ. The matrix

$$U(P)_{lm}=\langle SM,l|P|SM,m\rangle \qquad (24)$$

is a nonreducible representation matrix of the $N!$-element permutation group S_N. Several efficient algorithms of evaluating its elements are available.[18,24]

D. Eigenvalues and moments

The method of constructing the Hamiltonian matrix described above [Eqs. (19)–(24)] is a special case of a general approach referred to as SGA (symmetric group approach).[18] Recently a configuration-interaction program based on SGA has been developed.[31,32] This program is used to generate and to diagonalize the Hamiltonian matrix.

The Coulomb and resonance integrals have been determined as follows. A basic set of integrals has been chosen as to give the best least-squares fit of the theoretical and experimental spectra of benzene.[33] All experimentally known (four singlet and four triplet) electronic bands of benzene have been used in the fit. The theoretical energies have been found as exact solutions (full CI) of the PPP model.

The values of the integrals in the case of the benzene molecule are equal to[28]

$$\begin{aligned}\gamma_{11}^B&=10.8400\text{ eV} ,\\ \gamma_{12}^B&=7.6038\text{ eV} ,\\ \gamma_{13}^B&=6.0311\text{ eV} ,\\ \gamma_{14}^B&=5.2982\text{ eV} ,\end{aligned} \qquad (25)$$

and

$$\beta_{12}^B=-2.6163\text{ eV} .$$

The carbon atoms in the benzene ring are numbered clockwise from 1 to 6 (thus $\gamma_{12}^B=\gamma_{23}^B=\gamma_{34}^B=\gamma_{45}^B=\gamma_{56}^B=\gamma_{61}^B$, $\gamma_{14}^B=\gamma_{25}^B=\gamma_{36}^B$, etc.). The differences between the energy levels (i.e., the excitation energies) do not depend upon β_{11} and the nearest-neighbor approximation, i.e., $\beta_{13}^B=\beta_{14}^B=0$, was assumed in determining the integral values (25).

In all calculations reported in this paper the γ_{kl} integrals are calculated for interatomic distances R_{kl} smaller than R_{14}^{B} (the largest distance between two carbon atoms in benzene) by linear interpolation between the benzene values (25). For distances larger than R_{14}^{B} a Coulomb-like behavior of the integrals is assumed, i.e.,

$$\gamma_{kl}=2\gamma_{14}^{B}/\rho_{kl} \ , \tag{26}$$

where $\rho_{kl}=R_{kl}/R_{12}^{B}$.

For the resonance integrals the empirical formula[29] is used,

$$\beta_{kl}=37.03e^{-2.65\rho_{kl}} \ . \tag{27}$$

The qth moment of the spectral density distribution is defined as

$$[M(N,K,S)]_q=\mathrm{Tr}\{[\underline{H}(N,K,S)-\bar{E}]^q\}/D(N,K,S) \ , \tag{28}$$

where $\underline{H}(N,K,S)$ is a matrix representation of $\hat{H}_{\mathrm{PPP}}$ in H_N^A and where

$$\bar{E}=\mathrm{Tr}[\underline{H}(N,K,S)]/D(N,K,S) \tag{29}$$

is the average energy. If $[E(N,K,S)]_i$, $i=1,2,\ldots,D(N,K,S)$ are the eigenvalues of $\underline{H}(N,K,S)$ then

$$M_q=\sum_{i=1}^{D}(E_i-\bar{E})^q/D \ , \tag{30}$$

where, for simplicity, the arguments N,K,S have been omitted. A comparison of the numbers given by Eqs. (28) and (30) may be considered as a test of correctness of the program.[34]

III. STATISTICAL DESCRIPTION OF THE HAMILTONIAN SPECTRA

The density $\tilde{\rho}(E)$ of the discrete spectrum $E_1,E_2,\ldots,E_D$ is represented by the discrete normalized frequency function

$$\tilde{\rho}(E)=D^{-1}\sum_{i=1}^{D}\delta(E-E_i) \ , \tag{31}$$

$$\int_{-\infty}^{\infty}\tilde{\rho}(E)dE=1 \ , \tag{32}$$

and the corresponding average energy $\bar{E}$ and the moments M_q are

$$\bar{E}=\int_{-\infty}^{\infty}E\tilde{\rho}(E)dE \ , \tag{33}$$

$$M_q=\int_{-\infty}^{\infty}(E-\bar{E})^q\tilde{\rho}(E)dE \ . \tag{34}$$

The normalized distribution function $\tilde{F}(E)$ is defined by integrating the frequency function

$$\tilde{F}(E)=\int_{-\infty}^{E}\tilde{\rho}(E')dE' \ . \tag{35}$$

If the distribution moments are known, the discrete frequency function may be approximated by a continuous frequency function $\rho(E)$ chosen so that a given number of the lowest moments calculated with both the functions are the same. Since eigenvalues of N-electron Hamiltonians in finite-dimensional spaces tend to be distributed in a Gaussian-like fashion,[5,6,14] we adopt the Gaussian function as a starting point and proceed to modify it to take into account the higher moments of the distribution. It is convenient to construct the continuous frequency function $\rho(E)$ in terms of the dimensionless variable

$$x=(E-\bar{E})/\sigma \ , \tag{36}$$

where $\sigma=M_2^{1/2}$ is the width (dispersion) of the spectrum. The frequency function may then be expanded in terms of Hermite polynomials[35]

$$\rho(x)=(2\pi)^{-1/2}e^{-x^2/2}\sum_j c_jH_j(x) \ , \tag{37}$$

where, in virtue of the orthogonality relationship for Hermite polynomials, the coefficients are given by

$$c_j=\frac{1}{j!}\int_{-\infty}^{\infty}H_j(x)\rho(x)dx \ . \tag{38}$$

However, $\int_{-\infty}^{\infty}x^k\rho(x)dx$ may easily be expressed in terms of $M_1,M_2,\ldots,M_k$. Then, c_j may also be expressed as a linear combination of M_k, $k\le j$. The resulting equation is known as the Gram-Charlier expansion.[35] If the series (37) is terminated after p terms, then

$$\int_{-\infty}^{\infty}(E-\bar{E})^q[\tilde{\rho}(E)-\rho(E)]dE=0 \tag{39}$$

for $q=0,1,\ldots,p$. In such a case the continuous function ρ is referred to as being the p-moment equivalent of $\tilde{\rho}$.

The χ^2 test is used as a measure of the quality of the p-moment approximation to the frequency function. The value of χ^2 is calculated in the following way. First, the Hamiltonian spectrum is normalized to the distribution with $\bar{E}=0$ (subtracting $\bar{E}$ from all energy levels) and $\sigma=1$ (dividing $E_i-\bar{E}$ by σ). Then the energy range is divided into r intervals $(-\infty,x_1),(x_1,x_2),\ldots,(x_{r-1},\infty)$ in such a way that

$$F_G(x_{k+1})-F_G(x_k)=D/r \ ,$$

where $F_G(x)$ corresponds to the standard Gaussian frequency function. If $\tilde{n}_k$ is the number of the Hamiltonian eigenvalues within the (x_k,x_{k+1}) interval and

$$n_k=F(x_{k+1})-F(x_k) \ , \tag{40}$$

where

$$F(x)=\int_{-\infty}^{x}\rho(x')dx' \ , \tag{41}$$

then

$$\chi^2=\sum_{k=1}^{r}(\tilde{n}_k-n_k)^2/n_k \ . \tag{42}$$

The value of χ^2 is then compared with χ^2_{crit} chosen to correspond to the 5% probability level.[36]

If $F(x)$ is a continuous distribution function the corresponding smoothed spectrum can be defined as the set of values x_i which satisfy

$$F(x_i)=(i-\tfrac{1}{2})/D \tag{43}$$

for $i=1,2,\ldots,D$.[7,15] A comparison of the real energy levels and those derived from the distribution function according to Eq. (43) leads to notions of the secular eigenvalue density and of fluctuations.[10] The secular density is defined by a small number of moments. If it is described correctly, the fluctuations are small, energy independent, and unsensitive to increasing the value of p.

Finally, the last quantity being studied is the spacing between adjacent eigenvalues. As is known,[1,13,14] the spacings between eigenvalues belonging to the same symmetry species are distributed according to the Wigner distribution law

$$W(d)=\frac{\pi}{2}d\exp(-\pi d^2/4)\ , \tag{44}$$

where $d=s/\bar{s}$, s is the spacing and $\bar{s}$ is the mean value of s. The eigenvalues of different symmetries are not correlated and, in consequence, a superposition of several sets of different symmetry eigenvalues leads to an exponential distribution of spacings

$$x(d)=\exp(-d)\ . \tag{45}$$

As has been demonstrated already by Rosenzweig and Porter,[1] these rules may be used to study approximate (or hidden) symmetries. If, beyond the symmetry explicitly taken into account (say the total spin S), there exists another one (say the point-group symmetry of the molecular core), then the spacing distribution in fixed-S sequences either remains exponential or (if the other symmetry is approximate only) is an intermediate between the Wigner and the exponential form.

IV. RESULTS AND DISCUSSION

In Fig. 1 the spectra derived from the Gaussian and from the five-moment Gram-Charlier distribution function according to Eq. (43) are compared with the exact spectra of the PPP Hamiltonians for two different hydrocarbon chains. It is seen that the smoothed (moment-generated) spectra reproduce rather well the exact ones, especially in the central parts of the spectra. The discrepancies in the area of the lowest and the highest eigenvalues are considerably reduced if the number of moments taken into account increases. This observation is consistent with the earlier findings for atomic spectra.[15] A similar behavior of the nuclear spectra[7,10] indicates that in a very large class of quantum systems spectra derived from the low-moment distribution functions may be used as reasonable approximations to the real spectra. The same behavior of the spectra of the PPP Hamiltonians is illustrated in Fig. 2. The histogram of the Gaussian and the five-moment Gram-Charlier expansion is compared with the exact PPP frequency function for the singlet energy levels of the Hamiltonian describing the π-electron system of hexadiene. The deviations of the moment-generated spectra from the exact spectra, in the five-moment case, hardly exceed 0.1 eV, a quantity much smaller than the errors occurring in most advanced model calculations for this kind of quantum system.

It is rather well established that statistical properties of spectra depend rather strongly on the kind of interactions between particles.[4,8,10] However, numerical studies on this subject are rather scarce.[10,13,37] One of the aims of this study is to investigate the dependence of the form of the moment-generated spectra on the mutual relation between the interelectron interaction and the interaction of the electrons with the external potential of the molecular core. For this purpose we have recalibrated the resonance integrals introducing

$$\beta'_{kl}=B\beta_{kl}\ , \tag{46}$$

where B varies from 0 to ∞. In the case of $B=0$ the interelectron repulsion is the only interaction in the system. The role of the molecular core is reduced to creating the boundary conditions for the electron charge distribution. The case of $B=1$ corresponds to the physical reality—an interplay of one-body and two-body interactions. Finally, in the case of very large B, the interelectron interaction is negligible and effectively a system of noninteracting particles is moving in an external field.

In Fig. 3 deviations between the Gaussian and the exact singlet spectra of the benzene ($K=N=6$) PPP Hamil-

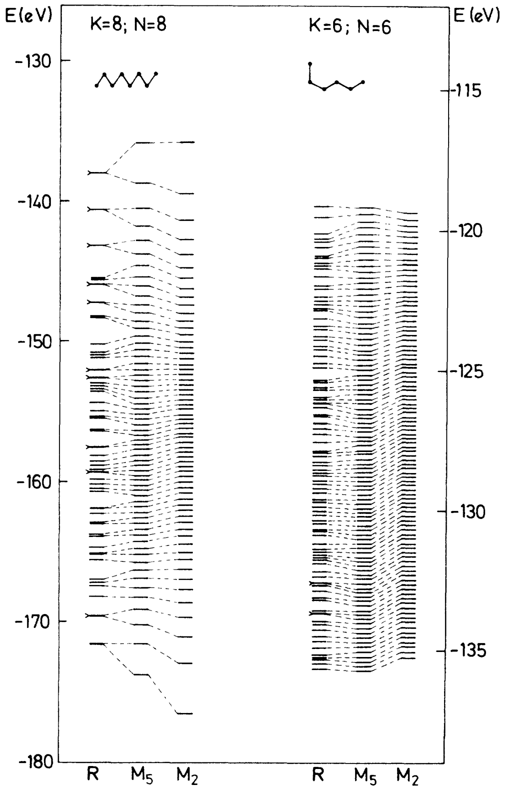

FIG. 1. The real PPP model spectra (R) and the moment-generated (M_p) spectra derived from them using Eq. (43). The distribution function, $F(x_i)$, is calculated in terms of p low-order spectral moments using Eqs. (37) and (41). The first example shows a complete 96-dimensional spectrum of the $N=K=8$ polyene in the $S=3$ spin state and the second example shows the central part (95 levels) of a 175-dimensional spectrum of the $N=K=6$ chain forming an "open benzene ring" in the $S=0$ spin state.

tonian are displayed. It can be seen that the deviations for $B=0$ are very large. In this case the spectrum is certainly non-Gaussian. Also for $B=\frac{1}{2}$ and for $B=10$, deviations from the normal distribution are much larger than for $B=1$. An even more distinctive illustration of the same problem is given in Fig. 4. Plots of $\chi^2/\chi^2_{\text{crit}}$ versus B are displayed for two rather different cases. The hypothesis that the frequency function is either Gaussian or low-moment Gram-Charlier is not true ($\chi^2/\chi^2_{\text{crit}}>1$) for small values of B, when two-body interactions are dominant. In the "physical" region, where B is close to 1, the distribution is either Gaussian or nearly Gaussian. For very large values of B the distribution again departs from normality though the limit value of $\chi^2/\chi^2_{\text{crit}}$ for $B\rightarrow\infty$ is much smaller than for $B=0$. In principle, the one- and two-electron terms in many-electron Hamiltonians are independent of each other. In the cases studied so far[5,6,12,14,15] their mutual relation in real atoms and molecules leads to nearly Gaussian frequency functions. It would be interesting to check how universal this property is and, in particular, to make a search for systems with "non-Gaussian" spectra.

Another way of measuring the quality of the moment-generated spectra is to calculate the standard deviation δ between the spectrum derived from the distribution function and the exact spectrum. In Fig. 5 plots of δ as a function of the number of moments taken into account in the Gram-Charlier expansion are shown. The plots correspond to several different molecules, however, in all cases no significant improvement of the moment-generated spectra is found if more than four moments are used in the expansion. Hence, the secular behavior of the spectra under consideration may be described in terms of not more than the first four moments of the corresponding Hamiltonians. The dependence of the statistical "smoothness" of the spectrum on the number of unoccupied one-electron levels is shown in Fig. 6. The standard deviations of the two-electron system spectra in different potentials are plotted versus K (the number of carbon

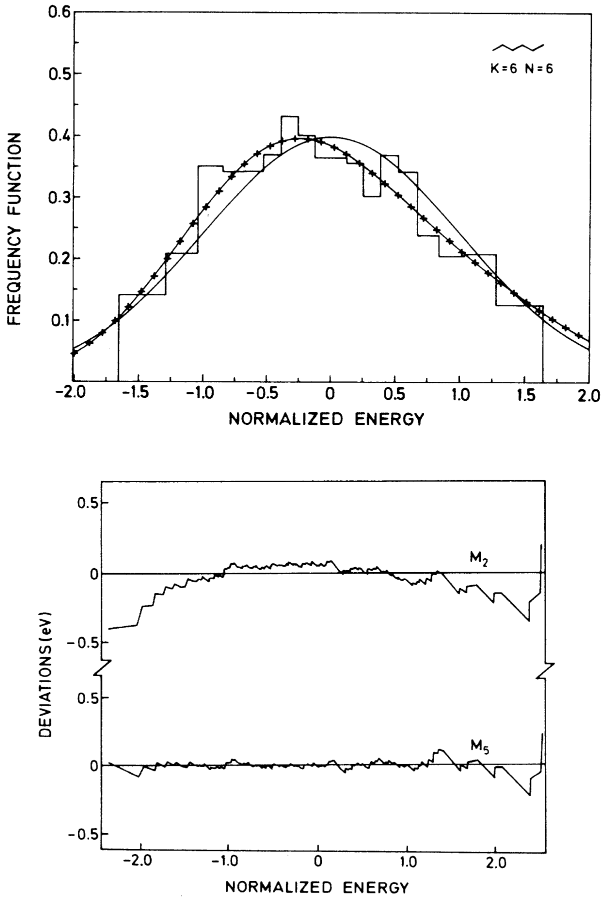

FIG. 2. In the upper part the histogram of the exact PPP frequency function $\tilde{\rho}(x)$ obtained for the $N=K=6$, $S=0$ polyene and the two- (——) and five-moment (+—+—+) Gram-Charlier expansions $\rho(x)$, are displayed. In the lower part the level-to-level deviations between the exact PPP spectrum and its Gaussian (M_2) and five-moment (M_5) versions are displayed.

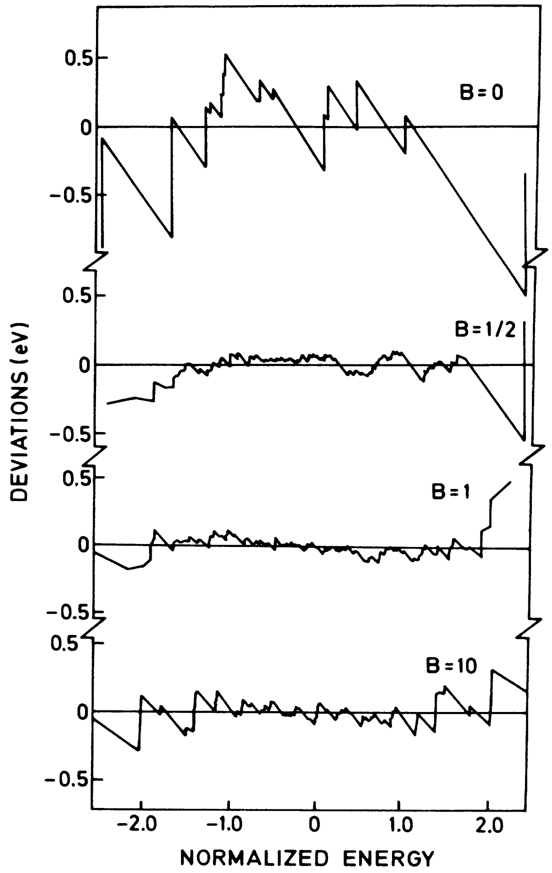

FIG. 3. Deviations between the exact PPP spectrum of the benzene molecule Hamiltonian for $S=0$ and its Gaussian versions. The spectra have been obtained using recalibrated values of the resonance integrals: $\beta'_{kl}=B\beta_{kl}$ with $B=0,\frac{1}{2},1,10$.

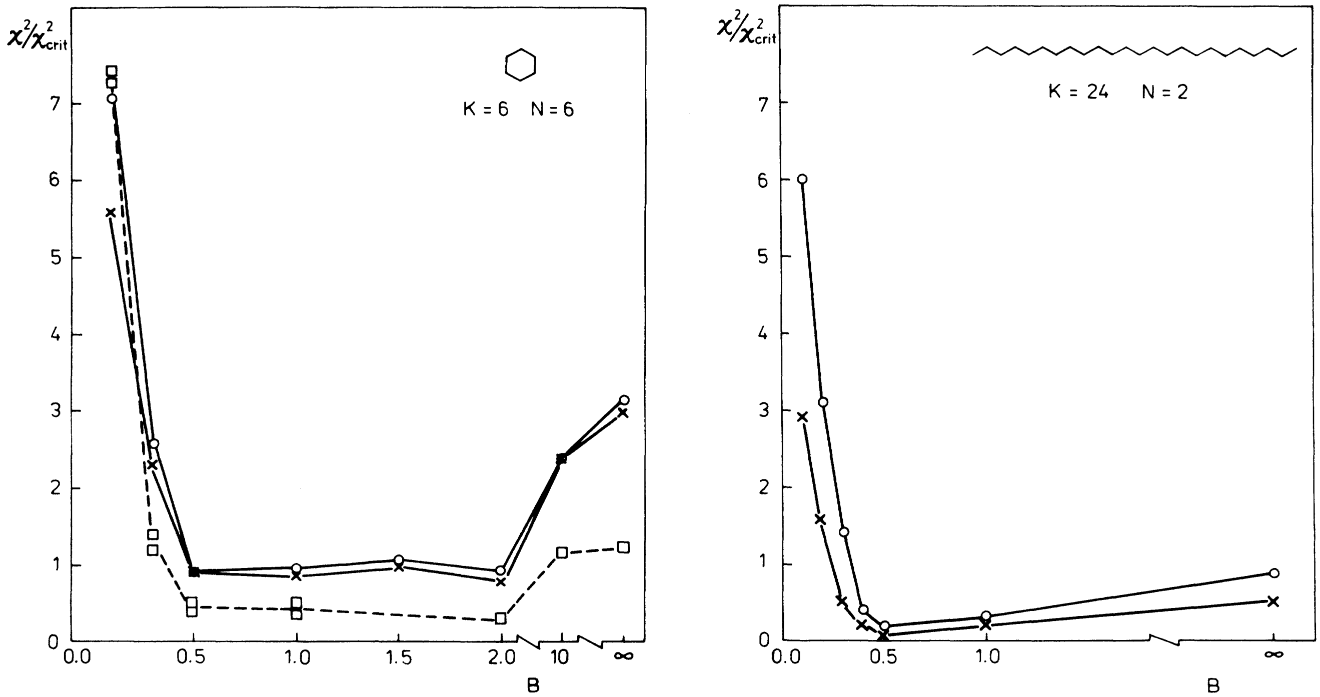

FIG. 4. The ratio of the calculated to the critical (for a 5% probability level) values of χ^2 for testing the Gram-Charlier secular density hypothesis applied to the exact PPP spectra. The spectra have been obtained using recalibrated values of the resonance integrals: $\beta'_{kl} = B\beta_{kl}$, where B is a variable parameter. The solid lines describe the behavior of the triplet and the dashed lines describe the behavior of the singlet manifolds of the energy levels versus B. For a given S the upper curve represents the Gaussian and the lower curve represents the nine-moment distribution case.

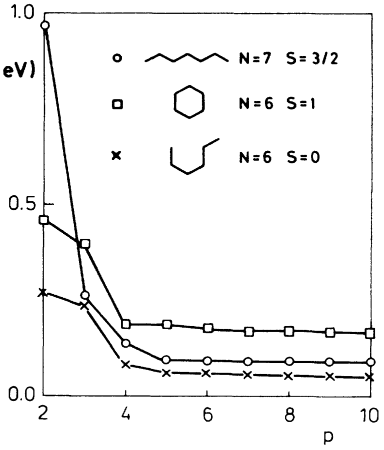

FIG. 5. Standard deviations δ (in eV) of the p-moment Gram-Charlier spectra from the exact PPP spectra vs p.

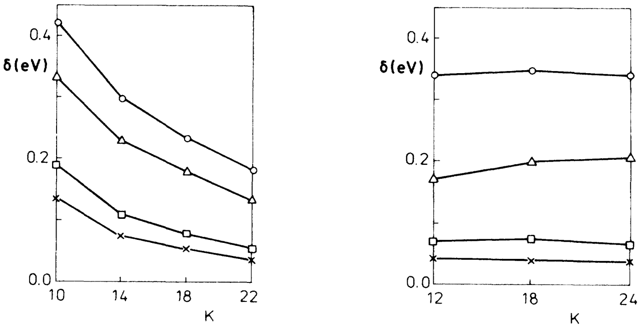

FIG. 6. Standard deviations δ (in eV) of the spectra generated by the p-moment Gram-Charlier expansions from the spectra obtained as exact solutions of the PPP model vs K (the number of carbon atoms). In the left-hand side of the figure the standard deviations of the singlet spectra of two electrons moving in the polyacene (naphtalene to pentacene) potential are displayed. In the right-hand side of the figure the same deviations, but for the triplet spectra of the linear polyenes, are displayed. The consecutive curves correspond to the two- (○——○), three- (△——△), four- (□——□) and ten-moment (×——×) Gram-Charlier expansions.

atoms, equal to the number of one-electron levels) for two-, three-, four-, and ten-moment Gram-Charlier expansions. For the singlet levels in polyacenes the distribution in the real spectra is becoming more smooth if K increases. However, for the triplet levels in polyenes almost no dependence of δ on K is observed. This last result is rather unexpected and needs further investigation.

The distributions of the spacings of the adjacent levels for several different systems are shown in Fig. 7. The results confirm the observations of many authors for nuclear,[10,11] atomic,[1,14,15] and molecular[13] spectra. Independently of the physical system, spacings between the energy levels corresponding to a single symmetry behave according to the Wigner distribution law (the right-hand side of Fig. 7) while the spacings between mixed symmetry levels are distributed according to the exponential law (the left-hand side of Fig. 7). The histograms are plotted for sequences of spacings between energy levels of the same spin ($S=0$). The molecular potentials corresponding to the distributions displayed on the right-hand side

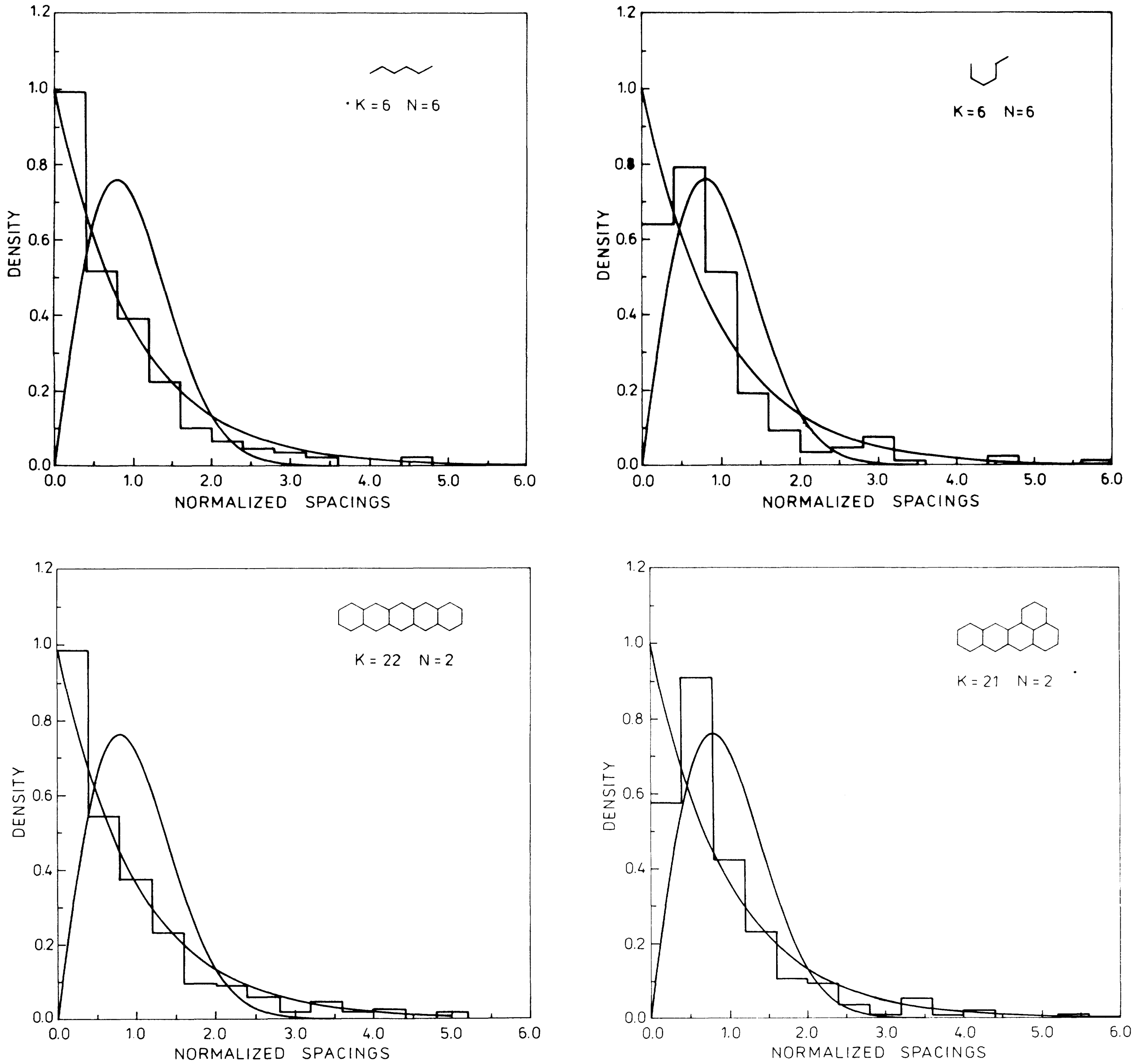

FIG. 7. The distributions of the adjacent level spacings in the exact $S=0$ PPP spectra compared to the Wigner and the exponential distributions.

of the figure do not have any other symmetry properties, while the two other potentials transform according to C_{2h} (upper left) and D_{2h} (lower left) symmetry groups. In the last two cases the singlet spectra are mixtures of energy levels corresponding to different irreducible representations of these groups.

ACKNOWLEDGMENTS

Partial support to M.B. and J.K. from the Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Contract No. CPBP.01.12. is gratefully acknowledged.

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