Semistochastic approach to many electron systems

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A Pariser–Parr–Pople (PPP) Hamiltonian of an 8π electron system of the molecule octatetraene, represented in a configuration-interaction basis (CI basis), is analyzed with respect to the statistical properties of its matrix elements. Based on this analysis we develop an effective Hamiltonian, which represents virtual excitations by a Gaussian orthogonal ensemble (GOE). We also examine numerical approaches which replace the original Hamiltonian by a semistochastically generated CI matrix. In that CI matrix, the matrix elements of high energy excitations are choosen randomly according to distributions reflecting the statistics of the original CI matrix.

I. INTRODUCTION

A proper description of interacting many-fermion systems still is one of the hard problems of modern chemistry and physics. A common approach to the description of many-fermion systems is an expansion of wave functions in terms of Slater determinants of one-particle functions. Such approach leads to high dimensional state (e.g., spin-coupled electron configurations) spaces, the dimensions of which increase exponentially with particle number. Consequently, computation times for evaluation of observables also increase drastically as a function of system size such that only small electron systems can be accurately described. In the case of molecular electronic systems the objective of such descriptions are the ground state and the lowest excited states.

In nuclear physics, and in some instances in atomic and molecular physics, the spectral region at higher energies and at high level densities has been investigated. It has been found for highly excited nuclei,[1] atoms,[2] and molecules[3] that in this spectral region many fermion configurations contribute to eigenstates, and that these states can be fairly well described by models which are based on statistical interactions (for a review see Ref. 4). In the high energy spectral region it is actually difficult to resolve single stationary states with definite quantum numbers. In the following such many-particle states are referred to as "complex" states. It is characteristic of such states, that their spectral properties depend weakly on the details of the interactions between single particle configurations[5] and one can assume that interaction matrix elements may have some random characteristics. This approach lends itself to a simplified description of spectra since statistical interaction models can be solved with considerably less computational effort than deterministic models.

In this paper we like to investigate to what extent stochastic models can be employed also for descriptions of low energy states of molecular many-electron systems. Our motivation for such investigation is that stochastic treatment of interactions between many-electron configurations may simplify the description of molecular electronic states. Such simplification is highly desirable since qualitatively correct and quantitatively accurate descriptions of electronic spectra of molecules require sophisticated and numerically complex many-electron methods.[6,7] As a first step in our investigation we examine to what extent statistical approaches yield correct descriptions of electronic excitations of conjugated molecules described by a Pariser–Parr–Pople (PPP) Hamiltonian. These excitations are known to exhibit strong electron correlation effects; as such they provide a good testing ground for new many-electron theories. The sample electron system which we consider is the π system of octatetraene which comprises eight electrons. This system, on the one hand, is large enough to allow statistical investigation and, on the other hand, is small enough to be calculated exactly.

In Sec. II we analyze the statistical properties of the elements of the configuration interaction matrix corresponding to a Pariser–Parr–Pople parametrization of the many-electron Hamiltonian. In Sec. III an effective Hamiltonian for the low-lying deterministic states is constructed. In this effective Hamiltonian statistical properties of the high energy complex states are represented by an ensemble averaged one-particle propagator (one-point function).[8] For a Gaussian orthogonal ensemble (GOE) which, like the PPP Hamiltonian, is orthogonally invariant, the one-point and the two-point functions were calculated by Verbaarschot, Weidenmüller, and Zirnbauer.[9] We analyze the existence of physical solutions of the eigenvalue problem for the effective Hamiltonian and present a self-consistent algorithm for a solution of the eigenvalue problem. In Sec. IV the spectrum of the effective Hamiltonian is compared to conventional, i.e., deterministic, PPP-CI spectra. In Sec. V a numerical approach is presented, in which we replace those matrix elements of the Hamiltonian involving higher excited electron configurations by random numbers, the

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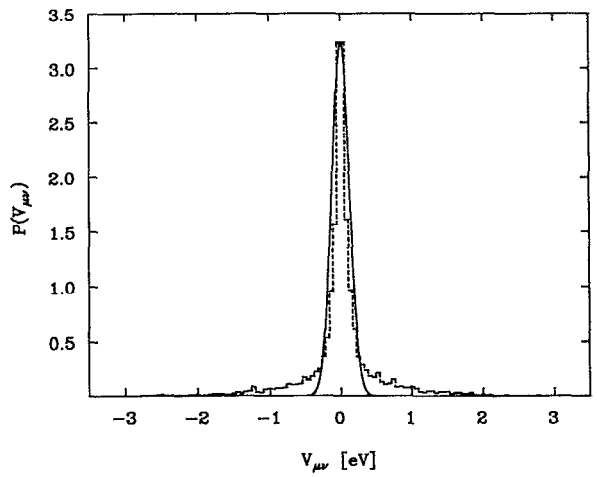

FIG. 1. Normalized distribution of all nonvanishing off-diagonal elements $V_{\mu\nu}$ of the PPP matrix (dashed line) and a Gaussian distribution (solid line). The variance of the Gaussian distribution has been chosen to be $\sigma^2 \approx 10^{-2}$ eV^2.

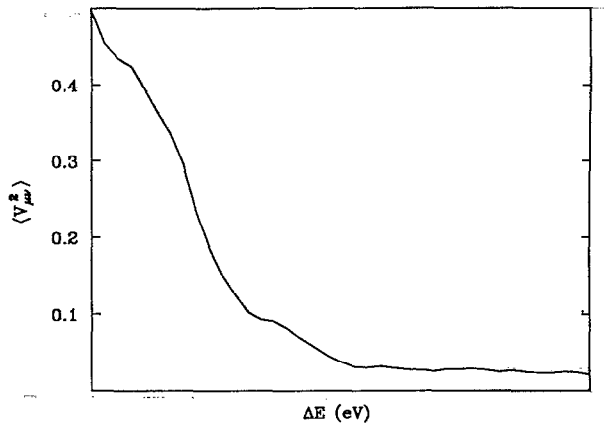

FIG. 2. Mean square of off-diagonal matrix elements $\langle V_{\mu\nu}^2 \rangle$ in units of eV^2. The ordinate is the energy difference $\Delta E = |V_{\mu\mu} - V_{\nu\nu}|$ of the corresponding diagonal elements.

distribution of which resembles those of the original matrix elements. The spectrum of the ensuing Hamiltonian is compared to that of the PPP-CI Hamiltonian. The paper is concluded by a summary.

II. STATISTICAL ANALYSIS AND DEFINITION OF THE MODEL

In this section we first provide a statistical analysis of the matrix elements of a PPP-CI matrix for octatetraene. The level assumed for the CI description includes up to four-particle–four-hole excitations (QCI).[7] That analysis serves to motivate a simple semistochastic model for the description of the PPP matrix, which is defined in the second paragraph.

A. Statistics of the PPP model matrix

First we analyze the statistics of the nonvanishing off-diagonal elements of the PPP matrix. The normalized distribution of these matrix elements is displayed in Fig. 1. It is slightly asymmetric around the origin with a mean value of $\langle V_{\mu\nu} \rangle \approx 0.008$ eV and a width of $\langle V_{\mu\nu}^2 \rangle = 0.255$ eV^2 for $\mu \neq \nu$. Because the mean value $\langle V_{\mu\nu} \rangle$ is $O(10^{-3})$, $\langle V_{\mu\nu}^2 \rangle$ is approximately equal to the variance with an error of $O(10^{-5})$, which is small compared to the width. The correlations between matrix elements $\langle V_{\mu\nu} V_{\mu'\nu'} \rangle$ are approximately 4×10^{-5} eV^2 ($\mu \neq \mu', \nu \neq \nu'; \mu \neq \nu', \nu \neq \mu'$), and thus vanish in a good approximation. The distribution displayed in Fig. 1 resembles a Cauchy distribution

$$P(V) = \frac{1}{2\pi\sigma} \frac{1}{1 + V^2/2\sigma^2}.$$

But all even moments $\langle \mathrm{Tr}\, V^{2n} \rangle$ for $n \geqslant 1$ of a Cauchy distribution diverge,[10,11] and we need for further calculation finite values of the second moments of the distribution of off-diagonal elements. Analytical calculations are feasible, however, for Gaussian distributions of matrix elements. Unfortunately, a Gaussian poorly reproduces the overall distribution of matrix elements in the PPP-CI Hamiltonian as illustrated in Fig. 1. Whereas the Gaussian approximates the matrix elements in the region near the maximum value well, it fails to represent matrix elements with large absolute values. The resulting Gaussian has a variance $\sigma^2 \approx 10^{-2}$ eV^2, which is much smaller than the variance $\sigma_{\mathrm{PPP}}^2 \approx \langle V_{\mu\nu}^2 \rangle = 0.255$ eV^2 ($\mu \neq \nu$).

Further details about the statistics of the off-diagonal elements $V_{\mu\nu}$ can be obtained if these matrix elements are divided into classes with fixed energy difference $\Delta E = |V_{\mu\mu} - V_{\nu\nu}|$ of corresponding diagonal elements. Figure 2 shows, that the width $\langle V_{\mu\nu}^2(\Delta E) \rangle$ of corresponding distributions $P(V_{\mu\nu}, \Delta E)$ of off-diagonal elements is monotonically decreasing with the energy difference ΔE of the respective diagonal elements. Hence, the ΔE-dependent distributions of off-diagonal elements are becoming smaller with increasing ΔE. The mean values $\langle V_{\mu\nu}(\Delta E) \rangle$ also depend on ΔE. For ΔE values in the range $\Delta E < 2$ eV the mean values are small and negative [$-O(10^{-2}$ eV)], for larger values of ΔE they are small and positive [$O(10^{-2}$ eV)].

The spectrum is the property of the PPP-CI matrix, which is of interest to us. For the purpose of describing properties of molecular systems under conditions prevailing in most chemical processes, only the lowest energy excitations are actually relevant. We will investigate, however, the complete spectrum of the PPP-CI matrix and its stochastic models. The reason is that such an analysis of the spectra of matrices with stochastic attributes reveals important characteristics of such matrices. We have determined therefore all eigenvalues E_j of the PPP-CI Hamiltonian studied, ordering them according to increasing energies. In Fig. 3 we present the result of such calculation, namely, the distribution of the differences between consecutive eigenvalues, i.e., $s = E_{j+1} - E_j$. Actually, Fig. 3 presents s in units of the mean level spacing $D = \langle E_{j+1} - E_j \rangle$. This distribution is compared to the Wigner distribution[5]

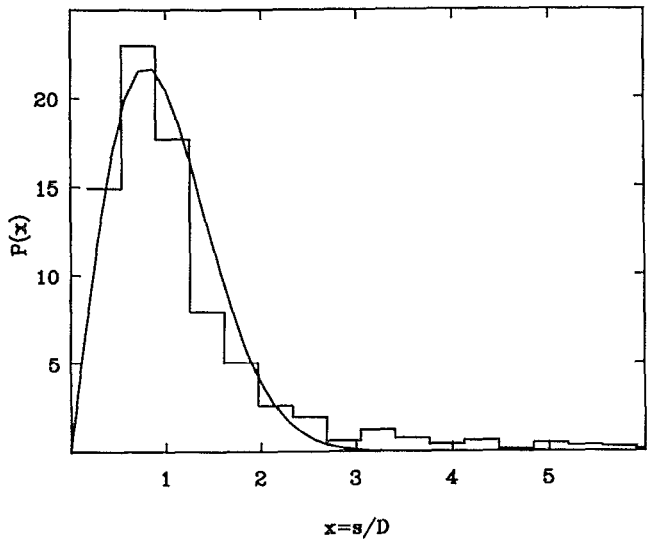

FIG. 3. Nearest-neighbor spacing histogramm of the 1195 PPP-CI eigenvalues as function of the relative level spacing $x=s/D$. That distribution is compared with a Wigner distribution ($D=0.0349$ eV).

$$P(s/D)=\frac{\pi s/D}{2}\exp\left[-\frac{\pi(s/D)^2}{4}\right],$$

which describes the spacing between consecutive eigenvalues for random matrices with matrix elements obeying a Gaussian distribution.

From Fig. 3 we can conclude, that neighboring many-particle levels of the PPP matrix repell each other, i.e., it is unlikely, that these levels are degenerate. This indicates correlations between the PPP levels at a scale of approximately one mean local spacing D. The repulsion between levels is due to the existence of nonvanishing off-diagonal elements of the PPP-CI Hamiltonian. Zimmermann *et al.*,[3] who investigated the optical absorption spectra of NO_2 and $C_2H_4^+$, have also found a Wigner distribution for the nearest-neighbor spacing of the many-particle levels of these systems. In contrast to such level repulsion, completely randomly distributed levels would tend to be degenerate representing a Poisson distribution. Zimmermann and Cederbaum have shown, that spectral statistics generally evolve continuously from regular to irregular fluctuations upon increase of the coupling.[12] Comparing with these results we find that our distribution of off-diagonal elements in Fig. 1 resembles a distribution which is typical for a weak-coupling case, whereas our distribution of level spacings in Fig. 3 appears to indicate strong coupling. In fact, the investigations in Ref. 6 have shown that the PPP model of polyenes corresponds to a case of intermediate coupling.

B. Analytical approximation of the PPP statistics

The distribution of energy level spacings $P(s/D)$ contains only information about fluctuations of the eigenvalue spectrum. The *global* behavior of the spectrum is determined by the number of possible combinations of many-particle states out of one-particle states.[13] In order to separate fluctuations from the mean behavior we divide the physical Hilbert space $\mathscr{H}$, the dimension of which in our case is $N_{\mathscr{H}}=1195$, into two subspaces. We introduce projection operators P and Q, which are orthogonal to each other ($P^2=P; Q^2=Q, P+Q=1$). As a consequence $\mathscr{H}$ can be expressed by the direct sum $\mathscr{H}=P\mathscr{H}\oplus Q\mathscr{H}$. The first subspace $P\mathscr{H}$ is spanned by the states with low energy. The dimension of this subspace is denoted as M. The second subspace $Q\mathscr{H}$ is spanned by the higher energy basis states. The dimension of $Q\mathscr{H}$ is $N=N_{\mathscr{H}}-M$, where $N_{\mathscr{H}}$ is the dimension of $\mathscr{H}$. The subspace $Q\mathscr{H}$ is the complement of $P\mathscr{H}$.

We now divide the PPP-CI Hamiltonian defined in $\mathscr{H}$ into one part H_0, which describes the deterministic and mean properties and another part V, which describes coupling to high energy virtual excitations and which we will refer to as the residual interaction

$$H=H_0+V=\begin{bmatrix} H_{ab} & \vdots & 0 \\ \cdots & \vdots & \cdots\cdots \\ 0 & \vdots & (\epsilon_\mu\delta_{\mu\nu}) \end{bmatrix}+\begin{bmatrix} 0 & \vdots & (PHQ)_{a\nu} \\ \cdots\cdots & \vdots & \cdots\cdots\cdots\cdots\cdots \\ (QHP)_{\mu b} & \vdots & (QHQ)_{\mu\nu}-(\epsilon_\mu\delta_{\mu\nu}) \end{bmatrix}. \tag{1}$$

The off-diagonal blocks in Eq. (1), $V_{a\nu}=(PHQ)_{a\nu}=[(QHP)_{\nu a}]^+$, can be considered as effective scattering potentials, which couple the deterministic and the stochastic regions by scattering low energy states into the space of virtual excitations and vice versa.

We choose the basis of eigenstates of H_0 as the basis in which we represent $\mathscr{H}$. In the following, states in $P\mathscr{H}$ are labeled by latin indices and states in $Q\mathscr{H}$ are labeled by greek indices:

$$H_0|\phi_a\rangle=E_{0a}|\phi_a\rangle \quad (|\phi_a\rangle\in P\mathscr{H}),$$

$$H_0|\phi_\mu\rangle=\epsilon_\mu|\phi_\mu\rangle \quad (|\phi_\mu\rangle\in Q\mathscr{H}). \tag{2}$$

An important starting point towards stochastic models of the Hamiltonian H is an energy ordering of the basis states $|\phi_\mu\rangle$, i.e., we assume $H_{\mu\mu}\leqslant H_{\nu\nu}$ for $\mu<\nu$. The function $h(\mu)=H_{\mu\mu}$ is then a monotonic function of μ. It is determined by the number of combinations a many-particle state can be formed out of single-particle states, a number which increases with energy. In the energy region of complex states, we approximate $h(\mu)$ by a continuous function with a smooth dependence on μ; the function with this property is ϵ_μ.

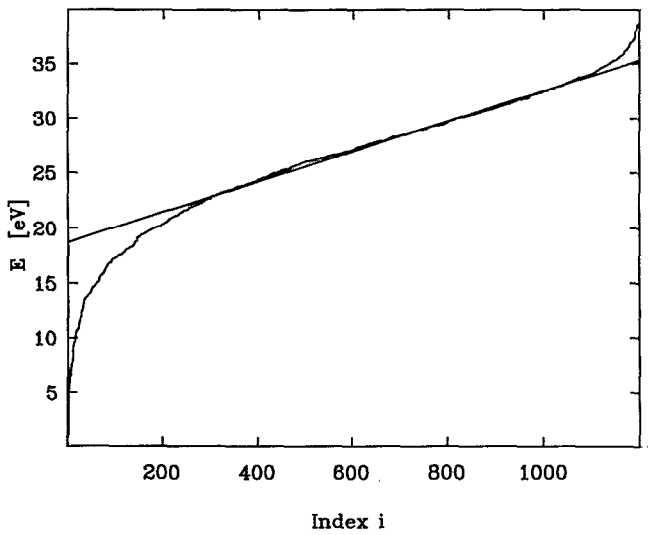

FIG. 4. Spectrum of the diagonal elements of the QCI-PPP Hamiltonian. High energy regions are approximated fairly well by $\epsilon_\mu = 20.1 + 0.014\mu$ (eV) (values $\mu = 1,..., N$, correspond to values $i = 101,..., N_{\mathscr{H}}$ of the index variable in the figure).

Let us briefly consider the relationship between $H_{\mu\mu}$ and ϵ_μ. Figure 4 shows the spectrum of energy-ordered diagonal elements of the QCI-PPP Hamiltonian. After a steep rise in the low energy region, the spectrum is approximately uniformly distributed, i.e., ϵ_μ increases linearly with μ, the latter corresponding to a constant density of states. We choose, therefore, the following approximation

$$\epsilon_\mu = \epsilon_{\min} + \mu d. \tag{3}$$

The parameters which, in case of the PPP-CI Hamiltonian, provide a good fit to $H_{\mu\mu}$ are $\epsilon_{\min} = 20.1$ eV, which can be interpreted as the lower energy boundary of $Q\mathscr{H}$, and $d = 0.014$, which represents the inverse of the mean energy density in $Q\mathscr{H}$ and provides a natural energy unit in this space. We have chosen the dimension M of the low energy state space such that all diagonal elements, which lie in $Q \times Q$ space, are well approximated by Eq. (3) and such that the mean value of the diagonal elements of the residual interaction $\langle V_{\mu\mu} \rangle$ vanishes. That choice renders $M = 100$ in our case.

We want to represent the off-diagonal matrix elements of H in $Q \times Q$ space, $V_{\mu\nu} = (QHQ)_{\mu\nu} - (\epsilon_\mu \delta_{\mu\nu})$ for $\mu \neq \nu$ which couple only complex states, by a random matrix. To derive such representation one considers H to be described as an ensemble of stochastic matrices.

Which mathematically tractable matrix ensembles share some properties with the PPP matrix? In order to find an answer we recall that there are two different units of energy: the mean local spacing D of *eigenvalues* and the local spacing d of the *diagonal elements*. A comparison of D with d can provide information about the coupling strength of the off-diagonal matrix elements. In the case of vibrations of polyenes, Jost[14] found the behavior ($1/D \approx 1/d$) as indicative for weak coupling. Since in case of the π-electron system described by the PPP-CI matrix the density of eigenvalues $1/D \approx 29$/eV is smaller than the density of diagonal elements $1/d \approx 71$/eV, the off-diagonal elements considerably affect the spectrum of the matrix. As mentioned above, that statement does not imply that the π-electrons represented by the PPP Hamiltonian are a strongly coupled system. It merely serves to obtain an estimate on the couplings within the CI matrix in the chosen basis which is made up of spin-adapted antisymmetrized products of Hartree–Fock one-electron states.

We want to consider now a representation of H by a particular ensemble of random matrices, namely, that referred to as a Gaussian orthogonal ensemble (GOE).[5] The GOE shows the same level repulsion as the PPP spectrum (cf. Fig. 3). In this respect the GOE is well adapted to the PPP-CI Hamiltonian in the $Q\mathscr{H}$ space. The GOE representation exhibits a strong coupling of matrix elements. Nevertheless, the distribution of off-diagonal matrix elements $V_{\mu\nu}$ is poorly approximated by a Gaussian (cf. Fig. 1).

In order to test, if the long-range correlations between the matrix elements in $Q\mathscr{H} \times Q\mathscr{H}$ space behave similar to those of the GOE, Δ_3 statistics has to be investigated (for a review see Refs. 4 and 15). Because of the high numerical effort this is left for future research. In this paper we employ the GOE as a simple analytically tractable model for the stochastic part of the PPP-CI Hamiltonian. Thus we are investigating the global influence, a stochastic model of the high lying states would have on the low lying states.

We assume the matrix elements of V to be "coordinates" of V in the "matrix-element space" $Q\mathscr{H} \times Q\mathscr{H}$. Then, V is represented as a vector in this space.

The GOE is defined in the space of real symmetric matrices by the following general assumptions:

(1) the matrix elements $V_{\mu\nu} (\mu \leqslant \nu)$ are independent random variables;

(2) the GOE is invariant under orthogonal transformations.

These general assumptions in a stochastic state space of dimension N lead to a uniform distribution of the matrix elements $V_{\mu\nu}$ with Gaussian shape[5]

$$P_N(V) = K_N \exp\left[-\frac{\mathrm{Tr}(V^2)}{4\sigma^2} \right].$$

Here K_N is a normalization constant. This distribution also follows from the condition of minimum information in the "matrix-element space" or from the assumption of a z_π-particle interaction.[5] Though a hypothetical z_π-particle interaction is unphysical, the GOE describes the fluctuation properties of nuclear spectra,[5] atomic spectra[2] and molecular spectra[3] quite well.

The first and second moments of a matrix ensemble described by a GOE are

$$\langle V_{\mu\nu} \rangle = 0, \tag{4a}$$

$$\langle V_{\mu\nu} V_{\mu'\nu'} \rangle = \sigma^2 (\delta_{\mu\mu'} \delta_{\nu\nu'} + \delta_{\mu\nu'} \delta_{\nu\mu'}), \tag{4b}$$

with $\sigma^2 = v^2/N$; v^2 depends on the number of interacting particles.

In our example of single, double, triple, and quadruple excitations of the 8π-electron system of octatetraene the approximation of the distribution of the off-diagonal elements by the GOE is so crude, see Fig. 1, that we determine v^2 by a Gaussian fit. It provides a variance of $\sigma^2 = v^2/N \approx 10^{-2}$ eV^2, i.e., $v \approx 4$ eV. We refer to such a modified "GOE" as an *extended GOE*.

Having defined a simple stochastic model for the matrix elements in the $Q\times Q$ part of the Hamiltonian, we now consider their coupling to the deterministic part by the matrix elements $V_{a\mu}$. The mean values $\langle V_{a\mu}\rangle$ are of the order $O(10^{-2}$ eV) (the average is solely over Q-space indices μ and ν]. Since the correlation between the P- and Q-space states increases monotonically with decreasing distance from the $P\mathscr{H}$ and $Q\mathscr{H}$ energy boundary, the functional form of the variance $\langle V^2_{\mu a}(\Delta E)\rangle$ (see Fig. 2) can, in a very crude way, be approximated by a simple exponential function of the index a

$$f_a = 0.01 e^{0.02a}, \tag{5}$$

with $f_0 = 0.01$ eV^2 and $f_{100} = 0.07$ eV^2. By using Eq. (5) and Fig. 4 a ΔE_a value can be associated to each index a. At the beginning of this section we have found, that the correlations between off-diagonal matrix elements are about 10^{-5} eV^2. The correlations between the scattering potentials $V_{\mu a}$ and $V_{\mu b}$ will be stronger and will tend to f_a for $|a-b|\to 0$. Thus if errors of the order $O(10^{-2}$ eV) are assumed to have a negligible influence on the results of our simple model, the coupling matrix elements between $P\mathscr{H}$ and $Q\mathscr{H}$ approximately can be assumed to be Gaussian distributed with vanishing mean values, i.e., we assume for the matrix elements

$$\langle V_{\mu a}\rangle = 0 \tag{6a}$$

and energy dependent variances

$$f_{ab} = \langle V_{\mu a} V_{\nu b}\rangle = \delta_{\mu\nu}\, e^{|a-b|} f_a. \tag{6b}$$

Equations (4), (5), and (6) define a simple model for the statistics of the matrix V, which permits an analytical treatment of the mean influence of complex states on the low lying states of the PPP matrix.

III. THEORETICAL METHODS (REF.17)

A. Effective Hamiltonian and secular equation

In a representation corresponding to the direct sum $P\mathscr{H}\oplus Q\mathscr{H} = \mathscr{H}$ the stationary states of the PPP-CI Hamiltonian are determined by

$$\begin{pmatrix} PHP & PHQ \\ QHP & QHQ \end{pmatrix}\begin{pmatrix} P\psi \\ Q\psi \end{pmatrix} = E\begin{pmatrix} P\psi \\ Q\psi \end{pmatrix} \tag{7}$$

for all $|\psi\rangle \in \mathscr{H}$. Since we are interested in states in the $P\mathscr{H}$ subspace, we solve the linear system in Eq. (7) in the form projected onto $P\mathscr{H}$

$$\left(PHP + PHQ\frac{1}{E-QHQ}QHP\right)P|\psi\rangle = EP|\psi\rangle. \tag{8}$$

In the preceding section we have divided H into H_0 and V [Eq. (1)] and have chosen the eigenbasis of H_0 [Eq. (2)] as the basis of $\mathscr{H}$. With respect to that basis the ith projected eigenvector in $P\mathscr{H}|\psi_P^{(i)}\rangle$ is given by

$$|\psi_P^{(i)}\rangle = P|\psi^{(i)}\rangle = \sum_{a\in P} c_a^{(i)}|\phi_a\rangle. \tag{9}$$

Eigenvalues and eigenvectors are solutions of Eq. (8) in the chosen basis[18]

$$[H^{\text{eff}}_{ab}(E_i) - E_i\delta_{ab}]c_b^{(i)}(E_i) = 0 \tag{10}$$

with an energy dependent effective Hamiltonian

$$H^{\text{eff}}_{ab}(E) = H_{ab} + \sum_{\mu\nu} H_{a\mu}\frac{1}{(E-QHQ)_{\mu\nu}}H_{\nu b}. \tag{11}$$

This resembles closely the block diagonalization procedure in Ref. 19. We want to use the statistical properties of the Hamiltonian, which we made plausible in the preceding section, to evaluate the eigenvalue problem [Eq. (10)]. In first order pertubation theory the averaging affects only the effective Hamiltonian and not the wave function. In second order pertubation theory the wave function would change and the averaging procedure would not be any more separable and would involve the two-point function. This is left for further investigation, here we want to provide a first guess for the influence of the highly excited states on the low lying ones. Thus in first order approximation, we are looking for global effects of the high lying complex states on the low lying deterministic states: The eigenvalue problem reduces to an eigenvalue problem of the ensemble averaged effective Hamiltonian. By construction the matrix elements $H_{a\mu} = V_{a\mu}$ and $(QHQ)_{\mu\nu} = V_{\mu\nu}$ are Gaussian distributed with vanishing mean values [Eq. (4) and Eq. (6)]. If we use the fact that for Gaussian distributed functions the mean value of the product equals the product of the mean values, we obtain for the statistical averaged effective Hamiltonian

$$\langle H^{\text{eff}}_{ab}\rangle = H_{ab} + f_{ab}\langle G(v,E)\rangle. \tag{12}$$

$\langle G(v,E)\rangle$ describes the influence of the complex part of the spectrum. Hence, the central problem of the calculation consists in the determination of the ensemble averaged propagator

$$\langle G(v,E)\rangle = \left\langle \sum_{\mu=1}^{N} [E-\epsilon_\mu - QVQ]^{-1}_{\mu\mu}\right\rangle = \langle \text{Tr}_\mu O^{-1}(E)\rangle \tag{13}$$

with

$$O_{\mu\nu}(E) \equiv [(E-\epsilon_\mu)\delta_{\mu\nu} - V_{\mu\nu}]. \tag{14}$$

B. Functional form of $\langle G\rangle$ and $1/N$ expansion

In order to determine the propagator $\mathrm{Tr}_\mu O^{-1}(E)$ we consider the generating function

$$Z(E,J)=\int_{-\infty}^{+\infty}\prod_{\mu'=1}^{N} d\phi'_\mu \exp\left[-\frac{i}{2}\sum_{\mu\nu}\phi_\mu O_{\mu\nu}(E)\phi_\nu + iJ\sum_\mu \phi_\mu^2\right], \tag{15}$$

which is related to the propagator through

$$\mathrm{Tr}_\mu O^{-1}(E)=\left.\frac{\partial \ln Z(E,J)}{\partial J}\right|_{J=0}. \tag{16}$$

Here ϕ_μ represent a set of real variables and J is a real-valued "source parameter." The logarithm of $Z(E,J)$ can be formally expressed through the limit $\lim_{n\to 0}(Z^n-1)/n$, where Z^n can be evaluated by means of the replica variables $\{\phi_\mu^k; k=1,\ldots,n; \mu=1,\ldots,N\}$ (Ref. 20)

$$Z^n(E,J)=\int_{-\infty}^{+\infty}\mathscr{D}[\phi]\exp\left[-\frac{i}{2}\sum_{\mu\nu k}\phi_\mu^k O_{\mu\nu}(E)\phi_\nu^k + iJ\sum_{\mu k}(\phi_\mu^k)^2\right], \tag{17}$$

with the common abreviation for the differential of path integrals: $\Pi_{\mu,k}[d\phi_\mu^k]=\mathscr{D}[\phi]$. This procedure, known as the "replica trick" had been introduced for the description of spin glasses[20,21] and in the present setting has been applied in Ref. 9.

Using the statistical properties of $V_{\mu\nu}$ (4) we obtain for the Green's function $\langle G(v,E)\rangle = \langle \mathrm{Tr}_\mu O^{-1}(E)\rangle$,

$$\begin{aligned}\langle G(v,E)\rangle &= i\lim_{n\to 0}\sum_{\alpha=1}^{N}\int_{-\infty}^{+\infty}\mathscr{D}[\phi](\phi_\alpha^l)^2\exp\left[-\frac{i}{2}\left\langle\sum_{k,\mu,\nu}\phi_\mu^k O_{\mu\nu}\phi_\nu^k\right\rangle\right]\\ &= i\lim_{n\to 0}\sum_{\alpha=1}^{N}\int_{-\infty}^{+\infty}\mathscr{D}[\phi](\phi_\alpha^l)^2\exp\left[-\frac{i}{2}\sum_{k,\mu}(E-\epsilon_\mu)(\phi_\mu^k)^2\right]\exp\left[-\frac{v^2}{4N}\sum_{k,k'}\left(\sum_\mu \phi_\mu^k\phi_\mu^{k'}\right)^2\right],\end{aligned} \tag{18}$$

for any fixed index l between 1 and n. In order to eliminate the quartic term in ϕ the real and symmetric auxiliary field variables $s_{kk'}(k,k'=1,\ldots,n; s_{kk'}=s_{k'k})$ are introduced (Hubbard–Stratonovitch transformation)

$$\begin{aligned}&\exp\left[-\frac{v^2}{4N}\sum_{kk'}\left(\sum_\mu\phi_\mu^k\phi_\mu^{k'}\right)^2\right]\\ &=c(n)\int\prod_{k<k'=1}^{n(n+1)/2} ds_{kk'}\exp\left[-\frac{N}{4}\sum_{kk'}(s_{kk'})^2\right]\\ &\quad\times\exp\left[\frac{i}{2}v\sum_{kk'}s_{kk'}\sum_\mu\phi_\mu^k\phi_\mu^{k'}\right].\end{aligned}$$

We note $c(n)=[(1/2)\sqrt{N/\pi}]^{n(n+1)/2}\to 1$ for $n\to 0$. If this expression is substituted back into Eq. (18) one obtains with $\mathscr{D}[s]=\Pi_{k<k'=1}^{n(n+1)/2}ds_{kk'}$

$$\begin{aligned}&\langle G(v,E)\rangle\\ &=i\lim_{n\to 0}c(n)\sum_{\alpha=1}^{N}\int_{-\infty}^{\infty}\mathscr{D}[\phi]\mathscr{D}[s](\phi_\alpha^l)^2\\ &\quad\times\exp\left[-\frac{N}{4}\mathrm{Tr}_k s^2\right]\exp\left[-\frac{i}{2}\sum_\mu\sum_{kk'}\phi_\mu^k[(E-\epsilon_\mu)\right.\\ &\quad\left.\times\delta_{kk'}-vs_{kk'}]\phi_\mu^{k'}\right].\end{aligned} \tag{19}$$

The integration over the ϕ_α^l, which now appear in a quadratic form, is formally straightforward. With the identity

$$\begin{aligned}&i\sum_\alpha(\phi_\alpha^l)^2\exp\left[\frac{i}{2}\sum_{\mu kk'}(\phi_\mu^k(s'_\mu)_{kk'}\phi_\mu^{k'})\right]\\ &=2\frac{\partial}{\partial s'_{ll}}\exp\left[\frac{i}{2}\sum_{\mu kk'}\phi_\mu^k(s'_\mu)_{kk'}\phi_\mu^{k'}\right]\end{aligned}$$

and partial integration over $(s'_\mu)_{kk'}=(E-\epsilon_\mu)\delta_{kk'}-vs_{kk'}$, giving rise to a term which tends to zero with n, the final form of the propagator reads

$$\begin{aligned}\langle G(v,E)\rangle=&\frac{N}{v}\lim_{n\to 0}c(n)(2\pi i)^{n/2}\int_{-\infty}^{\infty}\mathscr{D}[s]s_{ll}\\ &\times\exp\left[-\frac{N}{4}\mathrm{Tr}_k s^2-\frac{1}{2}\mathrm{Tr}_k\sum_{\mu=1}^{N}\ln\Omega_\mu\right],\end{aligned} \tag{20}$$

where $(\Omega_\mu)_{kk'}=(E-\epsilon_\mu)\delta_{kk'}-vs_{kk'}$ has to be strictly positive definite. Hence, the mean propagator is the expectation value of an $n\times n$ $(n\to 0)$-matrix field $s_{kk'}$, weighted with $e^{-\mathscr{L}(s)}$, where $\mathscr{L}(s)$ denotes the Lagrange function

$$\mathscr{L}(s)=\frac{N}{4}\mathrm{Tr}_k s^2+\frac{1}{2}\mathrm{Tr}_k\sum_{\mu=1}^{N}\ln[(E-\epsilon_\mu)\delta_{kk'}-vs_{kk'}]. \tag{21}$$

$\mathscr{L}(s)$ explicitly depends on the Q-space dimension N. Thus $\langle G\rangle$ can be expanded asymptotically in $1/N$. For $N\to\infty$ the mean (so-called classical) contribution, the saddle-point solution, is obtained.[8] The saddle point s_0 is given by $\partial\mathscr{L}/\partial s|_{s=s_0}=0$ as solution of the algebraic equation

$$s_0=\frac{v}{N}\sum_{\mu=1}^{N}\frac{1}{E-\epsilon_\mu-vs_0}. \tag{22}$$

This equation yields $N-1$, N or $N+1$ solutions generically denoted by the same symbol s_0. Only that solution yields a saddle point, for which (i) the second term in a Taylor expansion of $\mathcal{L}$ is positive and (ii) further terms, which describe fluctuations around the saddle point, are small compared to the second term.

With $s_{kk'}=s_0\delta_{kk'}+s^{(1)}_{kk'}$ one obtains for the Taylor series of $\mathcal{L}$ around the saddle point[16]

$$\mathcal{L}(s)=\mathcal{L}(s_0)+\sum_{p=2}^{\infty}\frac{1}{p}\frac{\partial^p\mathcal{L}}{\partial s^p}\bigg|_{s=s_0}\mathrm{Tr}_k[s^{(1)}]^p$$

$$=\mathcal{L}(s_0)+\mathcal{Z}(s^{(1)}), \tag{23}$$

$\mathcal{L}(s_0)$is the mean Lagrange function

$$\mathcal{L}(s_0)=\frac{1}{4}Ns_0^2+\frac{1}{2}n\sum_{\mu=1}^{N}\ln(E-\epsilon_\mu-vs_0). \tag{24}$$

$\mathcal{Z}(s^{(1)})$is the Lagrange function for the fluctuating part

$$\mathcal{Z}(s^{(1)})=\frac{1}{2}c_2\mathrm{Tr}_k(s^{(1)})^2+\mathcal{Z}_1(s^{(1)}), \tag{25}$$

where

$$\mathcal{Z}_1(s^{(1)})=\frac{1}{2}\sum_{p=3}^{\infty}\frac{c_p}{p}\mathrm{Tr}_k(s^{(1)})^p, \tag{26}$$

$$c_2=\frac{1}{2}N\left[1-\frac{1}{N}\sum_{\mu}\left(\frac{v}{E-\epsilon_\mu-vs_0}\right)^2\right], \tag{27}$$

and

$$c_p=\sum_{\mu}\left(\frac{v}{E-\epsilon_\mu-vs_0}\right)^p \quad \text{for } p\geq 3. \tag{28}$$

Substituting expression (23) into Eq. (20) one obtains a "loop"-expansion for the mean propagator[16]

$$\langle G\rangle=\frac{N}{v}\lim_{n\to 0}\Big\{d_0(n)s_0$$

$$+d_1(n)\int\mathcal{D}[s^{(1)}]s^{(1)}_{ll}\exp[-\mathcal{Z}(s^{(1)})]\Big\}$$

$$=\langle G_0\rangle+\langle G^{(1)}\rangle, \tag{29}$$

where

$$d_0(n)=\exp[-\mathcal{L}(s_0)]\int\mathcal{D}[s^{(1)}][-\mathcal{Z}(s^{(1)})]\to 1$$

for $n\to 0$,

$$d_1(n)=\exp[-\mathcal{L}(s_0)]\to 1 \quad \text{for } n\to 0.$$

Finally, $\exp[-\mathcal{Z}(s^{(1)})]$ is expanded into a power series in $1/N$

$$\exp[-\mathcal{Z}(s^{(1)})]=\exp\left[-\frac{c_2}{2}\mathrm{Tr}_k(s^{(1)})^2\right]$$

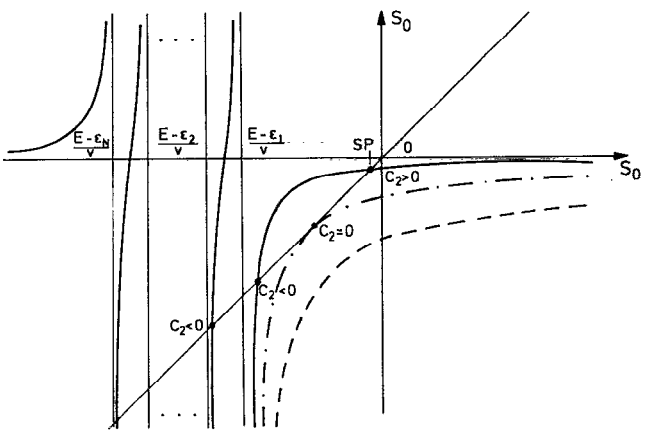

FIG. 5. Schematical graphical solution of the saddle-point equation (22). The solid line shows a typical hyperbola, in case Eq. (22) has $N+1$ solutions; the dot–dash line is the curve for N solutions and the case with $N-1$ solutions is dotted. The saddle point is marked with SP.

$$\times\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\mathcal{Z}_1^m(s^{(1)}). \tag{30}$$

Using the saddle-point equation (22) one obtains, to second order in $1/N$

$$\langle G(v,E)\rangle=\frac{N}{v}\left[s_0+\frac{c_3}{2c_2^2}+\frac{3c_5}{2c_2^3}+O\left(\frac{1}{N^3}\right)\right]. \tag{31}$$

C. Solution of the eigenvalue problem

The statistically approximated part of the matrix influences the deterministic part by an energy dependent propagator in the effective Hamiltonian [see Eq. (12)], which we derived in the preceding section for an extended GOE [Eq. (31)]. Now the eigenvalues of

$$H^{\mathrm{eff}}_{ab}(E)=H_{ab}+f_{ab}\frac{N}{v}\left(s_0+\frac{c_3}{2c_2^2}+\frac{3c_5}{2c_2^3}\right) \tag{32}$$

in the region of deterministic states

$$\frac{E-\epsilon_\mu}{v}<0 \quad \forall\epsilon_\mu \tag{33}$$

[see Eq. (2)] have to be calculated. First the solution of the saddle-point equation (22) is needed for the calculation of $H^{\mathrm{eff}}_{ab}(E)$.

Figure 5 shows schematically the $N-1$, N or $N+1$ solutions of Eq. (22), which exist for different parameters v. Only the solution with positive and maximal c_2 and with fluctuation coefficients c_3 and c_5 much smaller than $|c_2|$ is a saddle point. The stated conditions eliminate [see Eq. (27)] all solutions near the poles $s_0=(E-\epsilon_\mu)/v$ for which $c_2<0$. Thus only the solution closest to the origin on the branch at the extreme right of the graph is a saddle point. If the two lowest solutions are degenerate, i.e., $c_2=0$ (dot–dash curve in Fig. 5), the asymptotic expansion (20) diverges term by term.

Therefore, the existence of a saddle-point solution strongly depends on the variance v^2/N in the statistical

region. This constitutes the main difficulty in the selfconsistent diagonalization procedure for the effective Hamiltonian Eq. (32).

IV. SELF-CONSISTENT CALCULATION OF THE EFFECTIVE HAMILTONIAN'S EIGENVALUES

The eigenvalue problem for the energy-dependent effective Hamiltonian [Eq. (10)] has to be solved in a self-consistent way with given parameters H_{ab}, M, N, ϵ_μ, f_{ab}, v. For the P-space matrix elements H_{ab} we have chosen a 100×100 dimensional submatrix of the PPP matrix such that $\langle V_{\mu\mu}\rangle$ vanishes and ϵ_μ linearly increases in Q space (cf. Sec. II). Then, the dimension of the complementary, statistically described space is 1095. From the statistical analysis of the PPP matrix in Sec. II we obtained $\epsilon_\mu=\epsilon_{\min}+\mu d$ with $\epsilon_{\min}=20.1$ eV and $d=0.014$ eV [Eq. (3)]. The correlation between P and Q space is approximated by $f_{ab}=e^{-|a-b|}f_a$ with $f_a=0.01\,e^{0.02a}$ in units of [eV^2] [Eq. (5)], and the variance of our extended GOE $\sigma^2=v^2/N\approx10^{-2}$ eV^2 [Eq. (4)].

The algorithm of the self-consistent solution can be summarized in the following way:

(1) choose the ground state energy $E^{(0)}$, which satisfies the condition in Eq. (33);
(2) solve the saddle-point equation (22), with $c_2>0$, to obtain $s_0^{(0)}$;
(3) calculate the matrix elements of H^{eff} [Eq. (32)], which belong to $s_0^{(0)}$ and $E^{(0)}$;
(4) diagonalize H^{eff} [Eq. (10)].

Steps (1)–(4) have to be repeated for each eigenvalue which satisfies the condition in Eq. (33) up to self-consistency (E_i with $0\leqslant i<M$).

In Sec. III we have seen that the existence of a saddle-point solution strongly depends on the parameter v, i.e., on the distribution width of the matrix elements in Q space. Figure 6 shows a graphical solution of the saddle-point equation (22) in the region of $(E-\epsilon_{\min})/v<s_0<0$ for different parameters v. Figure 7 depicts corresponding values of c_2. If $v>6$ eV, no saddle point exists in the energy region of $E_0<E_i<\epsilon_{\min}$. If a saddle point exists, s_0 can only be in the range $-0.5\leqslant s_0<0$ (cf. Fig. 6). In this s_0 intervall c_2 is nearly constant with an approximate value of $c_2=N/2$. Therefore, the numerical value of the propagator depends only weakly on v.

For the parameter $v\approx4$ eV, which we obtained from the one Gaussian fit to the distribution of the CI off-diagonal elements, a saddle point exists. Therefore, the spectrum of the effective Hamiltonian [Eq. (32)] can be calculated by the self-consistent algorithm summarized further above. If the boundary between the deterministic and the stochastic region $\epsilon_{\min}$ is approached, the convergence of the self-consistent algorithm becomes worse, because then condition (33) allows only an approximation from the left. Furthermore, for that energy range the approximations for ϵ_μ in the region above the boundary and for f_{ab} in the region below are getting poorer.

Figure 8 shows the energies of the 50 lowest energy ordered eigenvalues for the 100×100 dimensional *deterministic* submatrix H_{ab}, for the effective Hamilton matrix

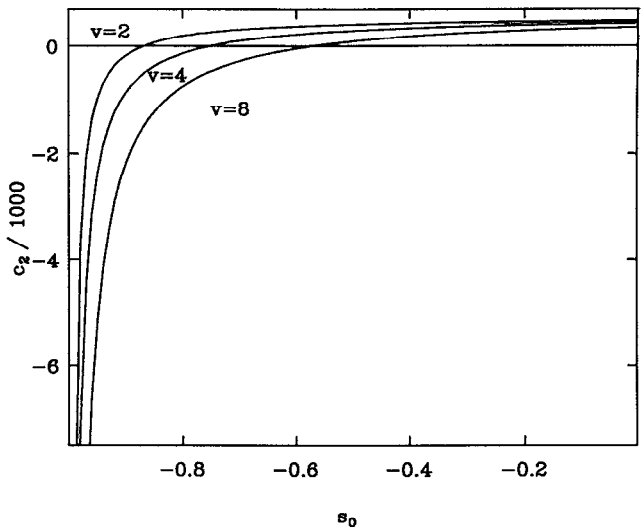

FIG. 6. Graphical solution of the saddle-point equation (22). The hyperbolas represent the right-hand side of the saddle-point equation for different parameters $v=2,4,8$ (from above), and energies E so that the pole of all graphs is located at $(E-\epsilon_{\min})/v=-1$.

H^{eff} and for the exact QCI-PPP Hamiltonian matrix. The eigenvalues of H^{eff} are evidently lowered relative to those of H_{ab}, but the QCI energies are still smaller than the H^{eff} energies except for the energy of the ground state. The ground state of H^{eff} lies at -1.445 eV, the QCI ground state at -1.4376 eV and that of H_{ab} at -1.009 eV.

Figure 9 shows the deviations of the eigenvalues of both H^{eff} and H_{ab} from the QCI-PPP eigenvalues. The ten lowest eigenvalues are reproduced with errors smaller than 0.5 eV. The lowering of the spectrum by the stochastic part of the matrix relative to H_{ab} increases as a function of the index. Particularly at high indices, this increase of the correlation correction does not suffice to reproduce the QCI-

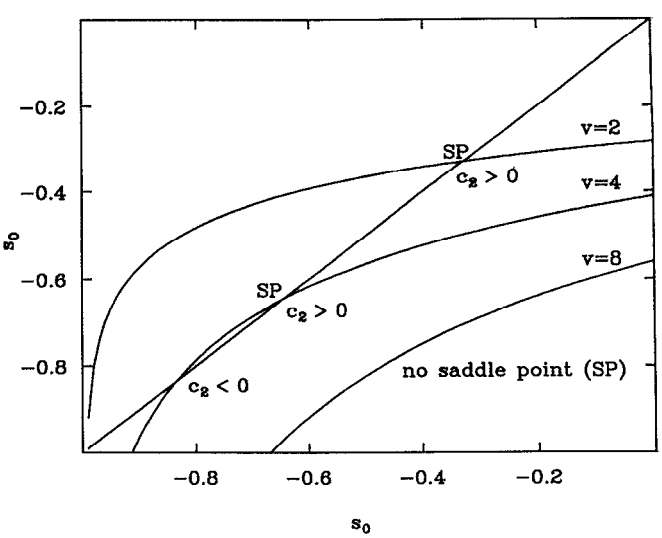

FIG. 7. Values of c_2 belonging to the parameter values in Fig. 6 in dependence of s_0 (from above, respectively).

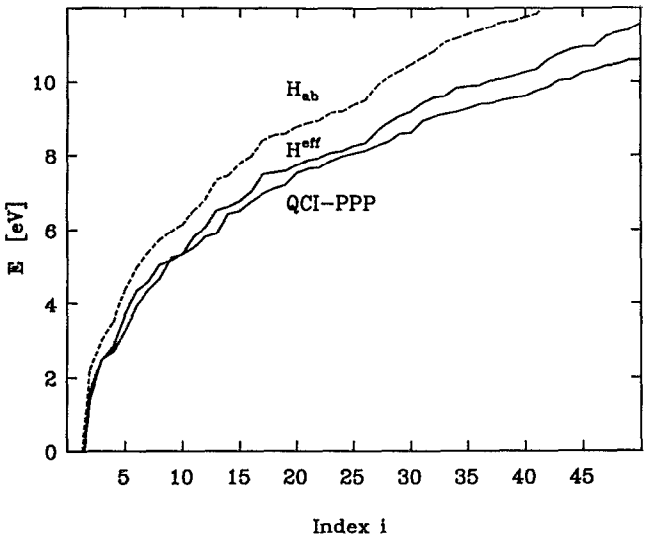

FIG. 8. The dashed curve represents the eigenvalue spectrum of the 100 $\times$100 dimensional submatrix H_{ab}, the solid curves the spectra of the effective Hamiltonian H^{eff} and of the exact QCI-PPP Hamiltonian matrix.

PPP spectrum.

As shown in Fig. 9 the fluctuations of the deviations of H^{eff} and of H_{ab} from the QCI eigenvalues proceed nearly parallel. Since for H^{eff} the deviations are much smaller than for H_{ab} we can infer that our rough statistical model describes global correlation corrections qualitatively correct. However, as indicated by the paralellism mentioned above, some of the more detailed correlation corrections, which are missing in the spectrum of H_{ab}, are also missing in the spectrum of H^{eff}. In that respect the spectrum of H^{eff} still reflects part of the effects which are due to the truncation of the CI space.

The failure in the description of these more detailed correlation effects is not surprising, because in our treatment we did not account for higher correlations of the PPP-CI matrix elements. Furthermore, in the analytical approximation [Eq. (11)] only first order perturbation theory and the one-point function, which takes care for a mean behavior, have been considered. To check for artifacts possibly introduced by some of the details of our model, we have employed several different test functions [Eq. (5)] to describe the coupling of the P and Q spaces. We found that the results are only weakly influenced by the functional description of the coupling matrix elements. Further investigations may answer the question, whether use of higher order pertubation theory and inclusion of longer range correlations in form of the two-point function can remedy the failures sketched above. The next section serves to exclude another possible source for the shortcomings of the simple model considered so far, that is the admittedtly crude approximation of the statistics of the off-diagonal elements by an extended GOE.

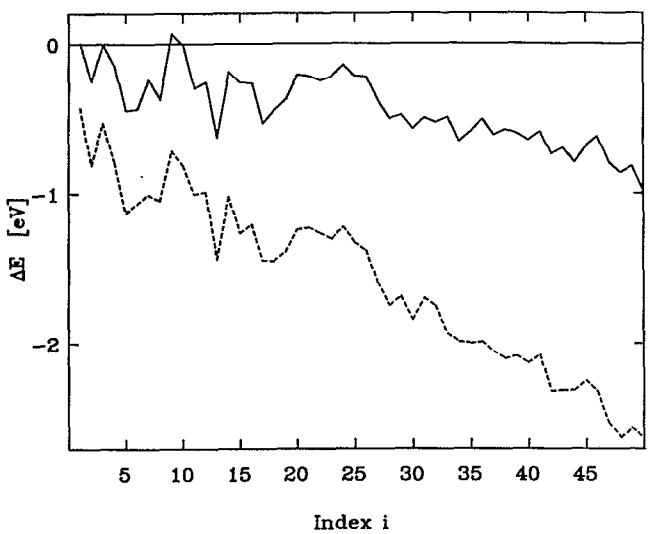

FIG. 9. Deviations of the 50 lowest eigenvalues of H^{eff} (solid lines) and of H_{ab} (dashed lines) from the exact QCI-PPP eigenvalues.

V. NUMERICAL ATTEMPTS

In the preceding section we have shown that a simple statistical model can provide a qualitatively correct description of the global influence of the complex states of a PPP matrix on the low energy states. However, that model failed to correctly reproduce the fine structure of the low-energy spectrum. In order to elaborate to what extent errors in the description of the lower energy states are due to the quality of the statistics in the stochastic state space, we employ a numerical model with improved statistics of the off-diagonal elements. Thus we try to approximate the distribution of off-diagonal matrix elements as closely as possible.

The statistics of off-diagonal elements, which depends on the energy difference of the diagonal elements ΔE, has been numerically reproduced by 40 individual random number generators for $0<\Delta E<20$ eV which approximate the empirical distributions $P(V_{\mu\nu},\Delta E)$ by two-Gaussian fitted distribution functions. Since we want to decrease the errors, caused by the neglect of deterministic correlation contributions, the dimension of the deterministic state space is considerably enlarged ($M=332$), so that the stochastic region extends deeply into the region of high level densities [cf. Fig. 4].

Figure 10 shows for the 50 lowest eigenvalues of the QCI matrix the differences to the corresponding eigenvalues of both the semistochastic matrix H_s ($M=332, N=863$) and of the deterministic submatrix H_d ($M=332$). Like in the case of the effective Hamiltonian, the inclusion of the stochastic part of the matrix into the calculation of the eigenvalues leads to a correlation correction. For the 20 lowest states that correction approximately assumes values between 0.02 und 0.15 eV and increases with energy (see Fig. 10). Similar to the case of the simple analytic approximation the *fluctuations* of the difference energies in Fig. 10 are not changed by inclusion of the stochastic part of the matrix. That shows that these fluctuations do not depend on the statistics chosen for the high energy part. As they derive from the reduction of the full deterministic

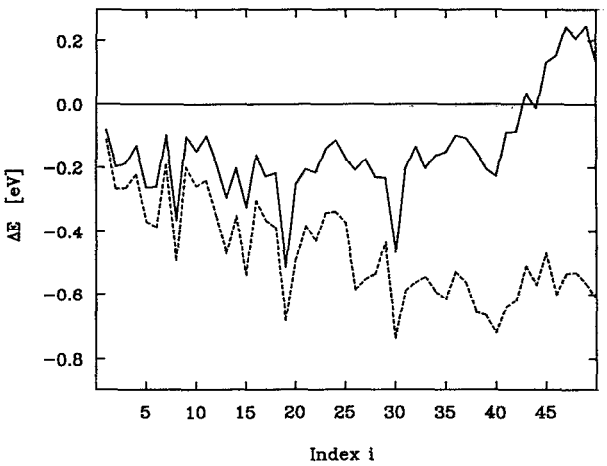

FIG. 10. Deviations of the 50 lowest eigenvalues of the semistochastic matrix H_s ($M=332$, $N=863$, solid lines) and of the deterministic submatrix H_d ($M=332$, dotted lines) from the exact QCI-PPP eigenvalues.

QCI space onto a less dimensional subspace, they reflect higher order correlations between matrix elements.

The errors of our numerically calculated semistochastic model, i.e., the deviations of statistically calculated from exact QCI state energies, amount to about 0.3 eV on the average. Due to the statistical choice of off-diagonal elements the eigenvalues of the semistochastic Hamiltonian have statistical errors of approximately 0.05 eV. The largest error for one of the ten lowest states is about 0.4 eV. Such error is too large for a quantitatively reliable description of the low-energy states of conjugated molecules, but it is small enough as to possibly enable a construction of a simple method to estimate the correlation effects of complex states even for larger molecules, for which spectra cannot be computed exactly.

VI. CONCLUSION

Taking an 8π-electron system as example, the suitability of simple semistochastic approaches for a description of the low-lying eigenvalues of many-electron systems has been analyzed.

The PPP-CI matrix has been divided into a low-dimensional deterministic submatrix, containing the low-energy states and a high-dimensional stochastic complementary matrix, which was approximated by an extended GOE. With this approach we calculated the eigenvalues of an energy dependent effective Hamiltonian in the deterministic state space. That Hamiltonian contains the contributions of the stochastic states in form of a propagator. The spectrum calculated in such a manner has been compared with the exact spectra of the PPP matrix and the spectrum of a deterministic submatrix (reduced CI).

The introduction of the propagator leads to a global correlation correction of the deterministic submatrix's eigenvalues. But, due to the truncation of the CI space large fluctuations are present in the correlation correction to level energies, which reflect higher order correlations between many-particle states and, hence, cannot be removed by our statistical approach. Therefore, the low energy eigenvalues of the CI matrix can only be qualitatively approximated by our simple statistical model. Nevertheless, about 80% of the correlation energy, caused by the complex states, are reproduced.

In order to analyze to what extent the results depend on the quality of the statistics for the stochastic part of the matrix, we have carried out a numerical investigation, in which the statistics of the PPP matrix elements in the high energy part of the matrix has been approximated by an ensemble of random number generators. Also this improved statistical approach renders only global correlation corrections to the spectrum of the low-energy deterministic part of the matrix. Large fluctuating deviations of about 0.3 eV from the exact level energies are still observed. Like in the simple analytical model these fluctuations arise from deterministic, higher order correlations among matrix elements that become neglected upon reduction of the CI space to a smaller, deterministic subspace.

Therefore, we conclude that a semistochastic method is appropriate if one is interested in a fast estimate of global correlation effects, caused by complex states. At present, the method is not well suited for an exact calculation of the low lying eigenvalues of the system. The system parameters—mean local spacing d and "lower boundary" of the stochastic space $\epsilon_{\min}$—can be extended to larger systems[6] where exact calculations are not available. Working out the behaviour of these parameters as a function of the system size is a task of further investigations.

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