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A class of exactly solvable matrix models

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Some exactly solvable matrix models are discussed. Possible applications to problems in physical chemistry are pointed out, in particular the Hückel problem, the problem of torsional vibrations of polyatomic molecules, and of vibrations of finite polymer chains.

1. Introduction

Several problems in quantum mechanics can be formulated in matrix form [3]. The eigenvalues and eigenvectors of the Hamiltonian matrices give the allowed energies and states. Although with the development of present day computers it has become possible to diagonalize numerically large matrices, it is still of interest to find explicit expressions for the eigenvalues and eigenvectors. The latter are particularly important since they can be used to calculate matrix elements of transition operators. Intensities of transitions can often be measured and they provide important information on the structure of a particular physical system. In this article, we generalize some known results for nearest neighbor matrices to include second neighbor matrices, full matrices and matrices that can be obtained by higher harmonic oscillator overtones. Our aim is to write down explicit expressions for the eigenvalues and eigenvectors of matrices of arbitrary sizes. These can be obtained in various ways. We use a recursive technique but the same results can be obtained using graph theory [1] or other techniques. For example, the spectrum of the ring matrices, R_n, discussed in section 2.2, corresponds to the spectrum of the cyclic graph, C_n, in graph theory, and it is given in table 4 of [1]. This result is valid for $n =$ even. For $n =$ odd and for the corresponding wave functions, see section 2.2. Similarly, the spectrum of the full matrices, K_n, for $n = 4$ is given in table 3 of [1]. Section 4 of this article gives the spectrum and eigenvalues for arbitrary n. We also mention briefly the connection between the eigenvectors of the matrices discussed here and the representations of finite groups. This connection has also been noted earlier [1]. In the last section we point out possible applications. The Hückel problem is also the standard application of graph theory, but torsional oscillations and polymer chains are of interest too. Finally, the main goal of this pa-

per is to provide the starting ground for the study of anharmonic systems. One of us (F.I.), together with Oss, has proposed [7] an algebraic model of anharmonic vibrations based on the Lie algebra $U(2)$. In the harmonic limit, this model reduces to the case briefly discussed in section 5. The solution for anharmonic vibrations, which relies on the results of the present paper, will be presented in a forthcoming publication [9].

2. Nearest neighbor matrices

2.1. Line matrices, M_N

The first set of matrices that we discuss are $n \times n$ matrices of the type

$$M_n = \begin{pmatrix} \alpha & \beta & 0 & 0 & \dots & 0 & 0 \\ \beta & \alpha & \beta & 0 & \dots & 0 & 0 \\ 0 & \beta & \alpha & \beta & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \beta & \alpha \end{pmatrix}, \tag{1}$$

where α, β are arbitrary real numbers, and columns and rows are labelled by $1, \dots, n$. These matrices arise, for example, in models of linear chains of coupled oscillators with nearest neighbor interactions (see figure 1). Solutions for this set of matrices are well known and have been obtained in a variety of ways. We consider here, for purposes of generalization, a recursive solution.

Since M_n is tridiagonal, its eigenvalues and eigenvectors can be found easily. The eigenvalues are obtained by solving

$$\det(M_n - EI_n) = 0, \tag{2}$$

where I_n is the unit $n \times n$ matrix. Denoting by $M'_n = M_n - EI_n$, one has the recursion relation

$$\det M'_n = (\alpha - E) \det M'_{n-1} - \beta^2 \det M'_{n-2}. \tag{3}$$

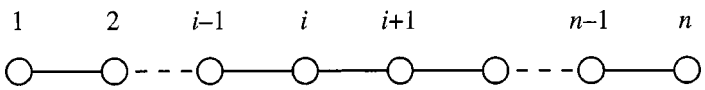

Figure 1. A linear chain of coupled oscillators.

But

$$\det M'_n = \det \left[\begin{pmatrix} \beta & 0 & 0 & \dots & 0 & 0 \\ 0 & \beta & 0 & \dots & 0 & 0 \\ 0 & 0 & \beta & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 0 & \beta \end{pmatrix} \times \begin{pmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & \dots & 0 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 & \dots & 0 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 1 & \frac{\alpha - E}{\beta} \end{pmatrix} \right]$$

$$= \beta^n \det \widetilde{M}_n, \tag{4}$$

where $\widetilde{M}_n$ is given by the second matrix in equation (4). The eigenvalue condition $\det M'_n = 0$ then becomes $\beta^n \det \widetilde{M}_n = 0$, which, for $\beta \neq 0$, gives

$$\det \widetilde{M}_n = 0. \tag{5}$$

The recursion relation for $\det \widetilde{M}_n$ ($n \geqslant 3$) can be simply obtained:

$$\det \widetilde{M}_n = \widetilde{\alpha} \det \widetilde{M}_{n-1} - \det \widetilde{M}_{n-2}, \tag{6}$$

where $\widetilde{\alpha} = (\alpha - E)/\beta$. By making the change of variable $E = \alpha - 2\beta \cos\theta$, we obtain

$$\det \widetilde{M}_n = 2 \cos\theta \det \widetilde{M}_{n-1} - \det \widetilde{M}_{n-2}, \tag{7}$$

whose solution is

$$\det \widetilde{M}_n = \frac{\sin(n+1)\theta}{\sin\theta}, \tag{8}$$

as one can easily verify by inserting (8) into (7). Condition (5) then gives the eigenvalues

$$(n+1)\theta = k\pi, \quad k = 1, 2, \dots, n, \tag{9}$$

and, hence,

$$E_k = \alpha - 2\beta \cos\theta_k, \quad \theta_k = \frac{k\pi}{(n+1)}, \quad k = 1, 2, \dots, n. \tag{10}$$

The eigenvectors can also be obtained and are given by

$$\psi_k = \frac{1}{\sqrt{N_k}} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}, \quad x_\nu = (-)^{n-\nu} \sin(\nu\theta_k), \quad \nu = 1, 2, \ldots, n, \tag{11}$$

with

$$N_k = \sum_{\nu=1}^{n} \sin^2(\nu\theta_k) = \frac{(n+1)}{2}. \tag{12}$$

When $n \to \infty$, θ_k goes continuously from 0 to π, and (4) leads to the well-known formula (dispersion relation)

$$E(\kappa) = \alpha - 2\beta\cos(\kappa a), \quad 0 \leqslant \kappa < \frac{\pi}{a}, \tag{13}$$

where a is a scale factor.

2.2. *Ring matrices, R_n*

Another set of matrices of interest is that composed of $n \times n$ matrices of the type

$$R_n = \begin{pmatrix} \alpha & \beta & 0 & 0 & \ldots & 0 & \beta \\ \beta & \alpha & \beta & 0 & \ldots & 0 & 0 \\ 0 & \beta & \alpha & \beta & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ldots & \vdots & \vdots \\ \beta & 0 & 0 & 0 & \ldots & \beta & \alpha \end{pmatrix}, \tag{14}$$

with α, β real. These matrices arise, for example, in models of rings of coupled oscillators with nearest neighbor interactions (see figure 2). (In graph theory [1], figure 2 is the cyclic graph C_n.) The eigenvalues and eigenvectors of the matrices

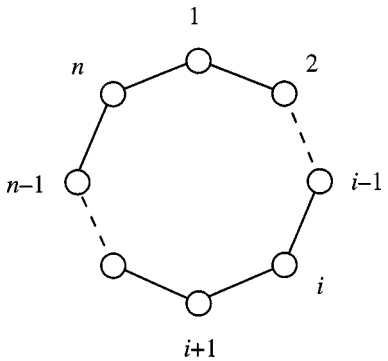

Figure 2. A ring of coupled oscillators.

R_n can also be obtained easily in closed form for any n. Introduce, as before, $R'_n = R_n - EI_n$. Then

$$\det R'_n = \det \left[\begin{pmatrix} \beta & 0 & 0 & \dots & 0 & 0 \\ 0 & \beta & 0 & \dots & 0 & 0 \\ 0 & 0 & \beta & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 0 & \beta \end{pmatrix} \begin{pmatrix} \widetilde{\alpha} & 1 & 0 & \dots & 0 & 1 \\ 1 & \widetilde{\alpha} & 1 & \dots & 0 & 0 \\ 0 & 1 & \widetilde{\alpha} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 1 & \vdots & \vdots & \dots & 1 & \widetilde{\alpha} \end{pmatrix} \right]$$
$$= \beta^n \det \widetilde{R}_n, \tag{15}$$

where $\widetilde{R}_n$ is given by the second matrix in (15) and $\widetilde{\alpha} = (\alpha - E)/\beta$ as before. The eigenvalue condition for $\beta \neq 0$ is here

$$\det \widetilde{R}_n = 0. \tag{16}$$

But now

$$\det \widetilde{R}_n = \widetilde{\alpha} \det \widetilde{M}_{n-1} - \det \begin{pmatrix} 1 & 1 & 0 & \dots & 0 & 0 \\ 0 & \widetilde{\alpha} & 1 & \dots & 0 & 0 \\ 0 & 1 & \widetilde{\alpha} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \widetilde{\alpha} & 1 \\ 1 & 0 & 0 & \dots & 1 & \widetilde{\alpha} \end{pmatrix}$$
$$+ (-1)^{n+1} \det \begin{pmatrix} 1 & \widetilde{\alpha} & 1 & \dots & 0 & 0 \\ 0 & 1 & \widetilde{\alpha} & \dots & 0 & 0 \\ 0 & 0 & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 1 & \widetilde{\alpha} \\ 1 & 0 & 0 & \dots & 0 & 1 \end{pmatrix}, \tag{17}$$

and the matrices on the right-hand side are $(n-1) \times (n-1)$. Changing $n-2$ times the rows and columns in the last determinant, one obtains the previous one. Thus,

$$\det \widetilde{R}_n = \widetilde{\alpha} \det \widetilde{M}_{n-1} - 2 \det \begin{pmatrix} 1 & 1 & 0 & \dots & 0 & 0 \\ 0 & \widetilde{\alpha} & 1 & \dots & 0 & 0 \\ 0 & 1 & \widetilde{\alpha} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \widetilde{\alpha} & 1 \\ 1 & 0 & 0 & \dots & 1 & \widetilde{\alpha} \end{pmatrix}. \tag{18}$$

Proceeding further,

$$\det \widetilde{R}_n = \widetilde{\alpha} \det \widetilde{M}_{n-1} - 2 \det \widetilde{M}_{n-2} + 2 \det \begin{pmatrix} 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & \widetilde{\alpha} & 1 & \dots & 0 & 0 \\ 0 & 1 & \widetilde{\alpha} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 1 & 0 & 0 & \dots & 1 & \widetilde{\alpha} \end{pmatrix}. \tag{19}$$

The last determinant can be reduced to $(-1)^{n-1}$ and thus one obtains the recursion relation ($n \geqslant 3$)

$$\det \widetilde{R}_n = \widetilde{\alpha} \det \widetilde{M}_{n-1} - 2 \det \widetilde{M}_{n-2} + 2(-1)^{n-1}. \tag{20}$$

Since we have already obtained $\det \widetilde{M}_n$ in the previous subsection, we have, upon substitution $\widetilde{\alpha} = 2\cos\theta$,

$$\begin{aligned} \det \widetilde{R}_n &= 2\left[\cos\theta \frac{\sin n\theta}{\sin\theta} - \frac{\sin(n-1)\theta}{\sin\theta} + (-1)^{n-1} \right] \\ &= 2\left[\cos n\theta - (-1)^n \right]. \end{aligned} \tag{21}$$

The eigenvalue condition (16) gives then the solutions

$$\theta = \begin{cases} \dfrac{2k\pi}{n}, & k = 1, 2, 3, \dots, n, \ n = \text{even}, \\ \dfrac{(2k+1)\pi}{n}, & k = 1, 2, 3, \dots, n, \ n = \text{odd}. \end{cases} \tag{22}$$

Reintroducing the eigenvalues E, we obtain

$$E_k = \alpha - 2\beta\cos\theta_k, \quad \theta_k = \begin{cases} \dfrac{2k\pi}{n}, & n = \text{even}, \\ \dfrac{(2k+1)\pi}{n}, & n = \text{odd}, \end{cases}$$

$$k = 1, 2, \dots, n, \ n \geqslant 3. \tag{23}$$

These eigenvalues are similar but *not* identical to those of the matrices M_n, the most notable difference being the factor of two in $2k\pi/n$ and the odd–even alternation. The eigenvectors can also be obtained. From (23) one can see that in this case there are eigenvalues which are not repeated and eigenvalues which are repeated *twice*.

(i) For the single eigenvalues we have the eigenvectors

$$\psi_k = \frac{1}{\sqrt{N_k}} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}, \quad x_\nu = (-1)^{n-\nu} \cos(\nu\theta_k), \quad N_k = \sum_{\nu=1}^{n} \cos^2(\nu\theta_k) = n/2. \tag{24}$$

(ii) For the double eigenvalues we have

$$\psi_k = \frac{1}{\sqrt{N_k}} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}, \quad x_\nu = (-1)^{n-\nu} \cos(\nu\theta_k), \quad N_k = \frac{n}{2},$$
$$\psi'_k = \frac{1}{\sqrt{N'_k}} \begin{pmatrix} x'_1 \\ x'_2 \\ \vdots \\ x'_n \end{pmatrix}, \quad x'_\nu = (-1)^{n-\nu} \sin(\nu\theta_k), \quad N'_k = \frac{n}{2}. \tag{25}$$

It is interesting to note at this stage that the resulting eigenvectors are (real) representations of the cyclic group C_n and that the method discussed here can be viewed as a convenient way to generate these representations no matter how large is n. Note also the odd–even alternation, which is not important for large n, but plays a major role for small n.

3. Second neighbor matrices

The set of matrices (1) arises in models of linear chains with nearest neighbor interactions. This set can be generalized to linear chains with second, third, etc. neighbor interactions. We consider here specifically the case of second neighbor interactions,

$$T_n = \begin{pmatrix} \alpha & 0 & \beta & 0 & \dots & 0 & 0 \\ 0 & \alpha & 0 & \beta & \dots & 0 & 0 \\ \beta & 0 & \alpha & 0 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 0 & \alpha \end{pmatrix}. \tag{26}$$

The recurrence relations for the determinants can also be solved in this case. The solutions provide the eigenvalue and eigenvectors. The eigenvalues can be written as

$$E_k = \alpha - 2\beta \cos\theta_k \tag{27}$$

as before. The values of θ_k are given by:

(i) $n =$ odd,

$$\theta_k = \frac{2k\pi}{(n+3)}, \quad k = 1, 2, \dots, \frac{(n+3)}{2} - 1,$$
$$\theta'_{k'} = \frac{2k'\pi}{(n+1)}, \quad k' = 1, 2, \dots, \frac{(n+1)}{2} - 1. \tag{28}$$

(ii) $n =$ even,

$$\theta_k = \frac{2k\pi}{(n+2)}, \quad k = 1, 2, \ldots, \frac{(n+2)}{2} - 1, \tag{29}$$

repeated twice.

The eigenvectors are:

(i) $n =$ odd,

$$\psi_k = \frac{1}{\sqrt{N_k}} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix},$$

$$x_{2\tau} = 0, \quad \tau = 1, 2, \ldots, \frac{(n-1)}{2},$$

$$x_{\tau'} = (-1)^{(n-\tau')/2} \sin\left[\frac{(\tau'+1)\theta_k}{2}\right], \quad \tau' = 2\rho + 1, \ \rho = 0, 1, \ldots, \frac{(n-1)}{2},$$

$$N_k = \frac{(n+3)}{4}, \tag{30}$$

and

$$\psi_{k'} = \frac{1}{\sqrt{N_{k'}}} \begin{pmatrix} x'_1 \\ x'_2 \\ \vdots \\ x'_n \end{pmatrix},$$

$$x_{2\tau+1} = 0, \quad \tau = 0, 1, \ldots, \frac{(n-1)}{2},$$

$$x_{\tau'} = (-1)^{(n-\tau'-1)/2} \sin\left(\frac{\tau'\theta'_{k'}}{2}\right), \quad \tau' = 2\rho', \ \rho' = 1, 2, \ldots, \frac{(n-1)}{2},$$

$$N_{k'} = \frac{(n+1)}{4}. \tag{31}$$

(ii) $n =$ even. In this case all roots are repeated twice. It is convenient to separate them and write the eigenvectors as

$$\psi_k = \frac{1}{\sqrt{N_k}} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix},$$

$$x_{2\tau} = 0, \quad \tau = 1, 2, \ldots, \frac{n}{2},$$

$$x_{\tau'} = (-1)^{(n-\tau'-1)/2} \sin\left[\frac{(\tau'+1)}{2}\theta_k\right], \quad \tau' = 2\rho+1,\ \rho = 0,1,\ldots,\frac{(n-2)}{2},$$
$$N_k = \frac{(n+2)}{4}, \tag{32}$$

and

$$\psi'_k = \frac{1}{\sqrt{N'_k}} \begin{pmatrix} x'_1 \\ x'_2 \\ \vdots \\ x'_n \end{pmatrix},$$
$$x_{2\sigma+1} = 0, \quad \sigma = 0,1,\ldots,\frac{(n-2)}{2},$$
$$x_{\sigma'} = (-1)^{(n-\sigma')/2} \sin\left[\frac{(\sigma')\theta'_{k'}}{2}\right], \quad \sigma' = 2\rho,\ \rho = 1,2,\ldots,\frac{n}{2},$$
$$N'_k = \frac{(n+2)}{4}. \tag{33}$$

Again it is important to note that, when $n \to \infty$, all eigenvalues are given by the same expression (27) with $\theta_k = 2\pi k/n$, to be compared with the eigenvalues of the matrices for nearest neighbor interaction ($\theta_k = \pi k/n$). However, major differences occur when n is small, as one can see from (28) and (29).

4. Full matrices

The last set of matrices that we discuss in this article is the set of $n \times n$ matrices

$$K_n = \begin{pmatrix} \alpha & \beta & \beta & \ldots & \beta & \beta \\ \beta & \alpha & \beta & \ldots & \beta & \beta \\ \beta & \beta & \alpha & \ldots & \beta & \beta \\ \vdots & \vdots & \vdots & \ldots & \vdots & \vdots \\ \beta & \beta & \beta & \ldots & \beta & \alpha \end{pmatrix}, \tag{34}$$

with α and β real. These matrices arise in models of coupled oscillators with equal interactions among *all* the oscillators. The eigenvalues and eigenvectors can be obtained directly from

$$\det(K_n - EI_n) = 0. \tag{35}$$

One can easily verify that the eigenvalues are

$$\begin{cases} E = \alpha + (n-1)\beta, & \text{singly degenerate,} \\ E = \alpha - \beta, & (n-1) \text{ times degenerate.} \end{cases} \tag{36}$$

The corresponding eigenvectors are:

(a) For the case $E = \alpha + (n-1)\beta$,

$$Y = \frac{1}{\sqrt{n}} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}. \tag{37}$$

This eigenvectors transforms as the totally symmetric representation (n) of S_n under permutation of the indices, with Young tableau [2]

$$(n) \equiv \overbrace{\square\square\ldots\square}^{n}. \tag{38}$$

(b) For the case $E = \alpha - \beta$, one can write $(n-1)$ independent vectors

$$X_1 = \begin{pmatrix} -(n-1) \\ 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \quad X_2 = \begin{pmatrix} 1 \\ -(n-1) \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \quad \ldots, \quad X_{n-1} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \\ -(n-1) \\ 1 \end{pmatrix}. \tag{39}$$

These vectors can be orthonormalized,

$$X'_1 = \begin{pmatrix} -\sqrt{\dfrac{(n-1)}{n}} \\ \dfrac{1}{\sqrt{(n-1)n}} \\ \vdots \\ \dfrac{1}{\sqrt{(n-1)n}} \end{pmatrix}, \qquad X'_2 = \begin{pmatrix} 0 \\ -\sqrt{\dfrac{(n-2)}{(n-1)}} \\ \dfrac{1}{\sqrt{(n-1)(n-2)}} \\ \vdots \\ \dfrac{1}{\sqrt{(n-1)(n-2)}} \end{pmatrix}, \qquad \ldots,$$

$$X'_{n-1} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ -\dfrac{1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} \end{pmatrix}. \tag{40}$$

They transform as the $(n-1)$-dimensional representation of S_n,

$$(n-1,1) = \begin{array}{c}\overbrace{\square\square\ldots\square}^{n-1}\\ \square\end{array}. \tag{41}$$

The eigenvectors (40) are not only orthogonal to each other but they are also orthogonal to the eigenvector Y. They can be used to generate a basis for the representations of S_n.

5. Generalizations. Nearest neighbor matrices

In order to generalize the class of exactly solvable matrices, we briefly revert to the algebraic form from which the matrices of sections 2–4 arise. (Models of this type are well known. See, for example, [10].) Introduce Bose creation and annihilation operators

$$\left[b_j, b_{j'}^\dagger\right] = \delta_{jj'}, \quad [b_j, b_{j'}] = \left[b_j^\dagger, b_{j'}^\dagger\right] = 0, \quad j, j' = 1, \ldots, n. \tag{42}$$

Write down the Hamiltonian

$$H = \alpha \sum_j b_j^\dagger b_j + \beta \sum_{j \neq j'} b_j^\dagger b_{j'} \tag{43}$$

and vacuum

$$|0\rangle \equiv \overbrace{|00\ldots0\rangle}^{n}. \tag{44}$$

The matrices of sections 2–4 are the representative matrices of H in the space of one boson (one quantum of vibration). We denote this space by $v = 1$. There are n basis states in this space. The jth state is

$$|1_j\rangle \equiv b_j^\dagger |0\rangle = |00\ldots1_j\ldots0\rangle. \tag{45}$$

Consider next the space with two quanta, $v = 2$. The two quanta can be either in the same oscillator

$$|2_j\rangle \equiv \frac{1}{\sqrt{2}} b_j^{\dagger 2} |0\rangle = |00\ldots2_j\ldots0\rangle, \tag{46}$$

or in different oscillators

$$|1_j 1_{j'}\rangle \equiv b_j^\dagger b_{j'}^\dagger |0\rangle = |00\ldots1_j\ldots1_{j'}\ldots0\rangle. \tag{47}$$

There are n states in (46) and $n(n-1)/2$ in (47) for a total of $n(n+1)/2$.

Since the Hamiltonian H can be diagonalized for any v by elementary methods, the matrices representative of H can also be exactly diagonalized. We list some typical cases.

5.1. *Line matrices,* $M_n^{(2)}$

The representative matrix, for $n = 3$, is

$$M_3^{(2)} = \begin{pmatrix} 2\alpha & \sqrt{2}\beta & 0 & 0 & 0 & 0 \\ \sqrt{2}\beta & 2\alpha & \beta & \sqrt{2}\beta & 0 & 0 \\ 0 & \beta & 2\alpha & 0 & \beta & 0 \\ 0 & \sqrt{2}\beta & 0 & 2\alpha & \sqrt{2}\beta & 0 \\ 0 & 0 & \beta & \sqrt{2}\beta & 2\alpha & \sqrt{2}\beta \\ 0 & 0 & 0 & 0 & \sqrt{2}\beta & 2\alpha \end{pmatrix}, \tag{48}$$

where the basis is labelled in the order $1^2, 12, 13, 2^2, 23, 3^2$. Matrices for n generic, $M_n^{(2)}$, can be constructed by taking matrix elements of H in the basis $1^2, 12, \ldots, 1n, 2^2, 23, \ldots, 2n, 3^2, \ldots, 3n, \ldots, n^2$, where 12 denotes the state with one quantum in oscillator 1 and one in 2, etc. The eigenvalues of these matrices are found to be

$$\begin{aligned} E_{k,k'} &= 2\alpha - 2\beta(\cos\theta_k + \cos\theta_{k'}), \quad k \leqslant k',\ k, k' = 1, 2, 3, \ldots, n, \\ \theta_k &= \frac{k\pi}{(n+1)}. \end{aligned} \tag{49}$$

In order to write down the corresponding eigenvectors it is convenient to use the algebraic notation of equations (42)–(44). In this notation, the eigenvectors ψ_k of (11) are written as

$$|\psi_k\rangle = \sum_j (-)^{n-j} \sin(j\theta_k)|0 \ldots 1_j \ldots 0\rangle. \tag{50}$$

Similarly, the eigenvectors of $M_n^{(2)}$ can be written as

$$\begin{aligned} |\psi_{kk'}\rangle = &\sum_{j<j'} \frac{(-)^{j+j'}}{\sqrt{2}} \left[\sin(j\theta_k)\sin(j'\theta_{k'}) + \sin(j\theta_{k'})\sin(j'\theta_k)\right] |0 \ldots 1_j \ldots 1_{j'} \ldots 0\rangle \\ &+ \sum_j \sin(j\theta_k)\sin(j\theta_{k'})|0 \ldots 2_j \ldots 0\rangle. \end{aligned} \tag{51}$$

The eigenvectors in (51), which correspond to the double vibration of a harmonic linear chain, are useful in the evaluation of anharmonic contributions to this chain (for example, by perturbation theory), as discussed in [9].

5.2. Ring matrices, $R_n^{(2)}$

The representative matrix, for $n = 3$, is

$$R_3^{(2)} = \begin{pmatrix} 2\alpha & \sqrt{2}\beta & \sqrt{2}\beta & 0 & 0 & 0 \\ \sqrt{2}\beta & 2\alpha & \beta & \sqrt{2}\beta & \beta & 0 \\ \sqrt{2}\beta & \beta & 2\alpha & 0 & \beta & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & 0 & 2\alpha & \sqrt{2}\beta & 0 \\ 0 & \beta & \beta & \sqrt{2}\beta & 2\alpha & \sqrt{2}\beta \\ 0 & 0 & \sqrt{2}\beta & 0 & \sqrt{2}\beta & 2\alpha \end{pmatrix}. \tag{52}$$

Matrices for n generic, $R_n^{(2)}$, can be constructed by taking matrix elements of H. They differ from those of A by additional non-zero elements due to the cyclic conditions. The eigenvalues of these matrices are found to be

$$\begin{aligned} &E_{kk'} = 2\alpha - 2\beta(\cos\theta_k + \cos\theta_{k'}), \quad k \leqslant k',\ k, k' = 1, 2, \ldots, n; \\ &\theta_k = \begin{cases} \dfrac{2k\pi}{n}, & n = \text{even}, \\ \dfrac{(2k+1)\pi}{n}, & n = \text{odd}. \end{cases} \end{aligned} \tag{53}$$

The corresponding eigenvectors can be constructed from those of section 2.2 in a way similar to that leading to (51). It is interesting to note that while the eigenvectors of section 2.2 transform as representations of the cyclic group C_n, those obtained here transform as products of representations of C_n. Second neighbor matrices can also be generalized but, since this generalization is straigthforward, we do not discuss it here.

6. Generalizations. Full matrices

The full matrices of section 4 can also be generalized. For $n = 3$, the matrix $K_3^{(2)}$ coincides with $R_3^{(2)}$. This is no longer the case for $n > 3$. Full matrices $K_n^{(2)}$ can be constructed again by taking matrix elements of H and they differ from the previous ones by having non-zero matrix elements $\langle j^2|H|jj'\rangle$ for any j'. The eigenvalues of these matrices for generic n are found to be

$$E = \begin{cases} 2\alpha + 2(n-1)\beta, & \text{singly degenerate}, \\ 2\alpha + (n-2)\beta, & (n-1) \text{ times degenerate}, \\ 2\alpha - 2\beta, & \dfrac{n(n-1)}{2} \text{ times degenerate}. \end{cases} \tag{54}$$

The corresponding eigenvectors transform as the following representations of S_n:

$$
\begin{aligned}
(n,0) &\equiv \square\square\ldots\square, && \text{single degenerate,}\\
(n-1,1) &\equiv \begin{matrix}\square\square\ldots\square\\ \square\end{matrix}, && (n-1)\text{ times degenerate,}\\
(n-2,2) &\equiv \begin{matrix}\square\square\ldots\square\\ \square\square\end{matrix}, && \frac{n(n-1)}{2}\text{ times degenerate,}
\end{aligned}
\tag{55}
$$

7. Further generalizations

The matrix representative of the Hamiltonian (43) for any number of quanta, v, and any number of oscillators, n, with nearest neighbour interactions and all interactions on a line and on a ring can be diagonalized in closed form. The generalization of the line and ring matrix solution is obvious and yields

$$
E_{kk'k''\ldots} = n\alpha - 2\beta \underbrace{(\cos\theta_k + \cos\theta_{k'} + \cos\theta_{k''} + \cdots)}_{v \text{ times}}, \tag{56}
$$

with $\theta_k, \theta_{k'}, \ldots$, as before. (This solution can also be obtained easily from the algebraic Hamiltonian (43).) The generalization of the full matrices K_n to $K_n^{(v)}$ can also be constructed from a knowledge of the representations of the permutation group, S_n, and their degeneracies. The representations that occur for a given v are $(n,0)$, $(n-1,1),\ldots,(n-v,v)$.

8. Applications

The results of sections 2–6 can be applied to the study of a variety of problems in physics and chemistry. In this article, we mention only a selected number of problems in physical chemistry.

8.1. Rings

8.1.1. Hückel problem

In the treatment of π orbitals in molecules such as formaldehyde, ethylene, and benzene, Hückel [5] introduced an approximate molecular orbital method which leads to a matrix representative of the Hamiltonian of the type discussed in section 3. (This is also the main application of graph theory [1].) In particular, for benzene, the matrix representative is R_6:

$$
R_6 = \begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & \beta\\
\beta & \alpha & \beta & 0 & 0 & 0\\
0 & \beta & \alpha & \beta & 0 & 0\\
0 & 0 & \beta & \alpha & \beta & 0\\
0 & 0 & 0 & \beta & \alpha & \beta\\
\beta & 0 & 0 & 0 & \beta & \alpha
\end{pmatrix}. \tag{57}
$$

The eigenvalues of this matrix can be simply obtained using (23) and are given by

$$E = \begin{cases} \alpha \pm 2\beta, & \text{singly degenerate,} \\ \alpha \pm \beta, & \text{doubly degenerate.} \end{cases} \tag{58}$$

The corresponding eigenvectors are

$$\begin{aligned} \psi^{(A)} &= \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6), \\ \psi^{(E_1)} &= \begin{cases} \frac{1}{\sqrt{12}}(\psi_1 - \psi_2 - 2\psi_3 - \psi_4 + \psi_5 + 2\psi_6), \\ \frac{1}{2}(-\psi_1 - \psi_2 + \psi_4 + \psi_5), \end{cases} \\ \psi^{(E_2)} &= \begin{cases} \frac{1}{\sqrt{12}}(-\psi_1 - \psi_2 + 2\psi_3 - \psi_4 - \psi_5 + 2\psi_6), \\ \frac{1}{2}(-\psi_1 + \psi_2 - \psi_4 + \psi_5), \end{cases} \\ \psi^{(B)} &= \frac{1}{\sqrt{6}}(-\psi_1 + \psi_2 - \psi_3 + \psi_4 - \psi_5 + \psi_6). \end{aligned} \tag{59}$$

Figure 3 shows the eigenvalues of equation (57). The eigenvectors here are representations of the cyclic group C_n. In the case of benzene, they are representations of C_6. The four distinct eigenvectors are the representations A (single degenerate), E_1 (doubly degenerate), E_2 (doubly degenerate) and B (singly degenerate). Using the results of section 7, Hückel problem can be solved for a ring of any arbitrary dimension, n.

In addition to the application to electronic configurations, generalizations of the matrix (57) have been used in the study of the vibrational spectroscopy of benzene (see, for example, [8]).

8.1.2. Torsional oscillations

In the problem of torsional vibrations of molecules (see, for example, [4]) such as toluene, phenol and ethylene one needs the solution of the wave equation (in dimensionless units)

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}\phi^2} + V(\phi)\right]\psi(\phi) = E\psi(\phi), \quad V(\phi) = \frac{1}{2}V_n(1 - \cos n\phi), \quad \phi \in [0, 2\pi). \tag{60}$$

The splitting of the degenerate levels in the potential (60) due to tunnelling through the barriers, figure 4, can be analyzed in matrix form. The matrices are R_n. For $n = 6$, a case of interest in toluene ($C_6H_5CH_3$), and nitromethane (CH_3NO_2), the solutions are as discussed in section 8.1.1. In order not to repeat that calculation, we consider here

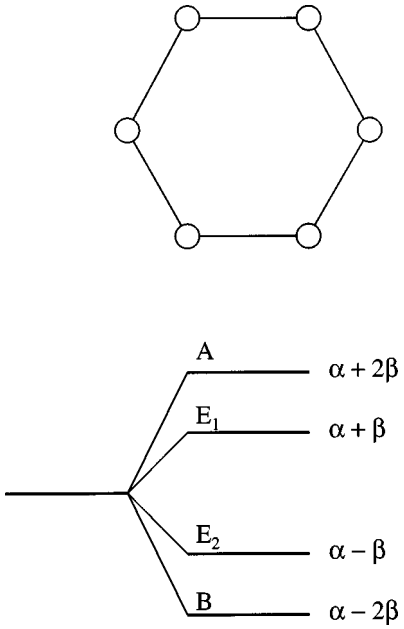

Figure 3. Splitting of degenerate electronic levels in a C_6 ring. The quantity β is usually negative.

the case of $n = 3$. This case is of interest in a variety of molecules, such as methyl alcohol and ethylene. The representative matrix is

$$R_3 = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}. \tag{61}$$

The eigenvalues of this matrix can be simply obtained using (23) and are trivially given by

$$E = \begin{cases} \alpha + 2\beta, & \text{singly degenerate,} \\ \alpha - \beta, & \text{doubly degenerate.} \end{cases} \tag{62}$$

The corresponding eigenvectors are

$$\begin{aligned} \psi^{(A)} &= \frac{1}{\sqrt{3}}(\psi_1 + \psi_2 + \psi_3), \\ \psi^{(E)} &= \begin{cases} \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 - 2\psi_3) \\ \frac{1}{\sqrt{2}}(-\psi_1 + \psi_2) \end{cases}. \end{aligned} \tag{63}$$

Figure 4 shows the eigenvalues of equation (62). The eigenvectors are representations of C_3. The singly degenerate eigenvector is the symmetric representation A and the doubly degenerate eigenvector is the representation E. Using the results of section 2.2,

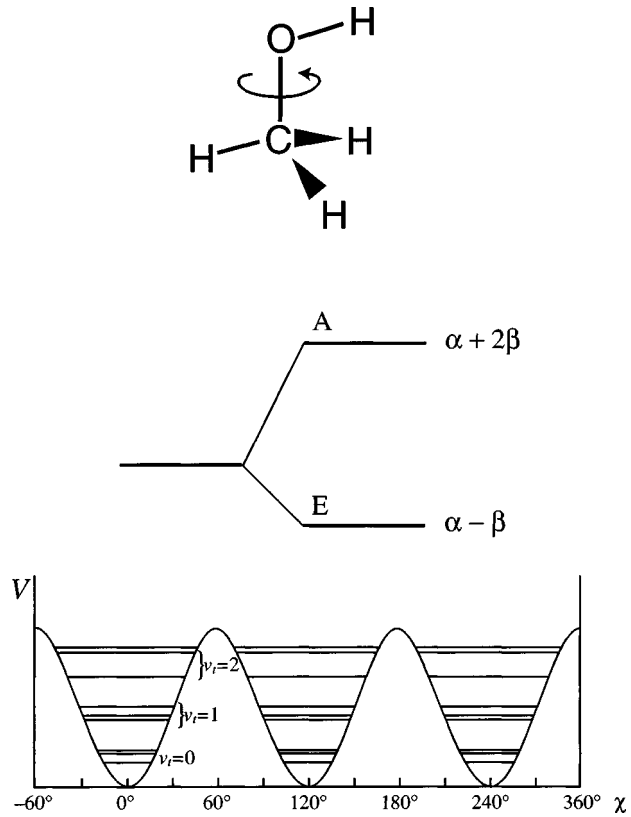

Figure 4. Splitting of degenerate torsional oscillations in metyl alcohol ($n = 3$).

the splitting pattern of degenerate levels due to barrier penetration can be obtained for a ring of any dimension, n.

8.2. Lines

In the study of finite polymer chains, Snyder [11] introduced a simple model of coupled harmonic oscillators which leads to matrix representatives of the type (1). In particular, Snyder studied the frequencies of methylene rocking and wagging modes in n-paraffins from n-$C_{20}H_{42}$ through n-$C_{30}H_{62}$. The matrix representations of the Hamiltonian for this series of paraffins are M_{20} through M_{30}. For nearest neighbor interactions, the energy eigenvalues are given by (10)

$$E_k = \alpha - 2\beta \cos\theta_k, \quad \theta_k = \frac{k\pi}{(n+1)}, \quad k = 1, 2, \ldots, n. \tag{64}$$

By studying the infrared spectra of paraffins in the range $n = 20$–30, it is possible to determine the coefficients α and β. Equation (64) can then be used to predict the frequencies in the range $n = 2$–20, where end effects become important, and for the infinite chain (polyethylene). If second neighbor interactions are included, the situation

is more complex, as shown in section 3. However, when n is large, the solution with both first and second neighbor interactions is approximately given by

$$E_k = \alpha - 2\beta_1 \cos\theta_k - 2\beta_2 \cos 2\theta_k, \tag{65}$$

where β_1 and β_2 represent the strengths of first and second neighbor interactions. The corrections to this formula are of order $1/n$ (compare equation (10) with equations (28) and (29)). The methods discussed in this article allow one to study this problem more accurately. They also allow one to study overtone and combination modes. The energy eigenvalues for these modes are given in sections 5 and 7:

$$E_{k,k'} = 2\alpha - 2\beta(\cos\theta_k + \cos\theta_{k'}), \quad k \leqslant k',\ k, k' = 1, 2, 3, \ldots, n,$$
$$\theta_k = \frac{k\pi}{(n+1)}. \tag{66}$$

9. Conclusions

In this article, we have given explicit expressions for the eigenvalues and eigenvectors of some finite and infinite dimensional matrices. These matrices appear in a variety of problems in physics and chemistry. Some of these applications have been indicated. The set of solvable matrices presented here is by no means complete and others can be found. Matrix models are closely related to algebraic models (see, for example, [6]), since the latter can always be represented in the space of matrices. Solvable matrix models thus imply solvable algebraic models and vice versa. The matrices presented here are related to the algebraic formulation of coupled one-dimensional harmonic oscillators (a relatively simple problem). By exploring further the connection between algebras and matrices, we have been able recently to provide solutions for a class of algebraic models describing coupled anharmonic oscillators. These results will be presented elsewhere [9].

Acknowledgements

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