Journal of Mathematical Chemistry 20 (1996) 273–283 

# Application of the Hill determinant approach to several forms of potentials in two- and three-dimensional quantum systems

M.R.M. Witwit

*Department of Applied Mathematics, University of Hull, HU6 7RX, UK*

Received 17 April 1996; revised 22 October 1996

Energy levels of the Schrödinger equation are calculated for several forms of potentials in two- and three-dimensional space and over a wide range of values of the perturbation parameters by means of the Hill determinant approach. The obtained numerical results are compared with those previously reported by other methods.

## 1. Introduction

In the past several years, much analytical and numerical work has been published on one-dimensional systems; however, the information about two- and three-dimensional systems is still relatively limited. The study of harmonic oscillators in higher dimensions is of interest not only for purely theoretical reasons but also from the point of view of applications in chemical physics and nuclear physics, for example in the study of intramolecular vibrational energy transfer [1–3], of the vibrational spectroscopy of polyatomic molecules intramolecular [4,5], and of unimolecular reactions [6].

In this paper we present some extended numerical calculations which use the Hill determinant technique (in an iterative form) to calculate the energy levels of the Schrödinger equation for some model potentials in two and three dimensions, for a wide range of values of the perturbation parameters and for several eigenstates. The technique has previously been applied to perturbed oscillator systems with an even parity perturbation [7,8]; in this work we intend to point out the flexibility of the Hill determinant in handling mixed parity perturbations.

The general form of the Schrödinger equation for several model potentials in multi-dimensional systems can be written as

$$\left[-\sum_{I=1}^{d}\beta\frac{\partial^2}{\partial x_I^2}+V_d(x_I;\lambda\ldots)\right]\Psi(x_I,\ldots)=E\Psi(X_I,\ldots)$$
$$(x_1=x,x_2=y,x_3=z;\beta=\tfrac{1}{2},1)\,. \tag{1}$$

Here and subsequently the coordinate indices run from 1 to $d$, the number of dimensions. The $\beta$ values are chosen to facilitate comparison with previous works.

The present paper treats three examples: the first system studied is the two-dimensional potential:

$$V_2(x, y; \lambda, \mu) = \tfrac{1}{2}[\omega_x^2 x^2 + \omega_y^2 y^2] + \lambda[xy^2 + \mu x^3]\,. \tag{2}$$

Recently there has been a great deal of interest in the analytical as well as the numerical study of the two-dimensional potential (2). Consequently, it is practically impossible to present a nearly complete list of references on the potential (2). Hence, we shall only quote references dealing with the accurate numerical evaluation of energy eigenvalues and with different summability techniques.

The energy levels of this potential have been calculated by semiclassical techniques as well as by quantum mechanical techniques [9–12]. The eigenvalues and wavefunctions of the potential using adiabatic approximation theory have also been calculated [13], and hypervirial perturbation theory combined with the adiabatic approximation has been used to calculate energy levels [14]. Perturbative semiclassical methods and the WKB approximation have also been used to treat the same potential [15,16]. The hypervirial perturbative approximation [17] has been used to study the same potential for several sets of perturbation parameters.

The potential (2) has no strictly bound quantum mechanical states (owing to tunnelling), though for small excitations the error in assuming discrete eigenvalues is small. The quantal energy spectrum of a nonintegrable Hamiltonian is expected to exhibit a characteristic behaviour; at low energies the energy levels belong to a regular spectrum, and at higher energies energy levels will exist belonging to an irregular spectrum. The energy levels of the irregular spectrum are more sensitive to a slowly changing or fixed perturbation than those of the regular spectrum.

In the case of a three-dimensional system, we consider two model potentials, the first one being

$$V_3^{\mathrm{m}}(x, y, z; \lambda, \eta, \mu, \xi) = \tfrac{1}{2}\left[\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right] + \lambda\left[xy^2 + \eta x^3\right] + \mu\left[yz^2 + \xi y^3\right], \tag{3}$$

where m means mixed parity perturbation.

The potential $V_3^{\mathrm{m}}(x, y, z; \lambda, \eta, \mu, \xi)$ has been previously treated by many researchers [16,18,19] using different techniques. For instance, Meyer et al. [18] and Noid et al. [19] used a semiclassical method to calculate the energy eigenvalues for several eigenstates. The eigenvalues calculated by the semiclassical method are compared with exact quantum eigenvalues, and the agreement is good.

As a second model, we consider a double well potential in a three-dimensional system:

$$V_3^{\mathrm{e}}(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda) = -Z_x^2 x^2 - Z_y^2 y^2 - Z_z^2 z^2 + \lambda\left[x^4 + y^4 + z^4 + 2x^2y^2 + 2x^2z^2 + 2y^2z^2\right], \tag{4}$$

where e means even parity perturbation.

The eigenvalue spectrum of the Schrödinger equation (1) with $V_3^e(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ has the feature that the lower eigenvalues are closely bunched in one group if the values of the $Z_{X_i}^2$'s are sufficiently large with small values of $\lambda$. As $Z_x^2$, $Z_y^2$ and $Z_z^2$ increase, the magnitude of the splitting between these levels decreases, i.e.

$$|E_{111} - E_{000}| \approx |E_{100} - E_{000}| \approx |E_{110} - E_{000}| \approx \Delta E \approx 0 . \tag{5}$$

## 2. The recurrence relation for the potential $V_2(x, y; \lambda, \mu)$ in a two-dimensional system

The traditional literature on Hill determinants deals with one-dimensional problems; the extension to two or three dimensions necessarily involves the use of a product basis set, leading to large matrix or determinantal problems, which are conveniently handled by a relaxation method.

Also the Hill determinant approach has been applied to several forms of potentials for important quantum systems [20,21].

In this section we use the Hill determinant approach to calculate the energy levels of quantum-mechanical systems with potential functions which have nonsymmetric behaviour. An extended analysis of numerical calculations is carried out for several model potentials in two- and three-dimensional systems; the results reveal the applicability of the Hill determinant approach for handling potentials in a multidimensional system.

To find the recurrence relations which allow us to calculate the eigenvalues for the Schrödinger equation (1), we introduce the wavefunction in the form

$$\Psi_{n_x,n_y}(x, y) = \exp -\tfrac{1}{2}[\alpha_x x^2 + \alpha_y y^2] \sum_{M,N} H(M, N)(x^M y^N) . \tag{6}$$

Substituting this wavefunction in the Schrödinger equation (1), we obtain, after some algebra, the following recurrence relation:

$$[(2\alpha_x M + 2\alpha_y N + \alpha_x + \alpha_y - 2E]H(M, N) = W(M, N) , \tag{7}$$

where

$$\begin{aligned} W(M, N) = {} & (M + 2)(M + 1)H(M + 2, N) + (N + 2)(N + 1)H(M, N + 2) \\ & + (\alpha_x^2 + \omega_x^2)H(M - 2, N) + (\alpha_y^2 + \omega_y^2)H(M, N - 2) \\ & - 2\lambda[H(M - 1, N - 2) + \mu H(M - 3, N)] . \end{aligned} \tag{8}$$

The recurrence relation (7) is used as follows. First the state numbers $n_x$ and $n_y$ (0, 1, 2, ...) are chosen, specifying which particular state is being treated, and

then the initial coefficient $H(M_0, N_0)$ is set equal to one, with $M_0 = n_x$ and $N_0 = n_y$.

In matrix-theoretic terms, the calculation is using a Gauss–Seidel ($R = 1$) or successive-over-relaxation ($R \neq 1$) approach to calculate the low eigenvalues of a large matrix. Increasing $M$ and $N$ corresponds to increasing the number of basis states, i.e., the dimension of the matrix. In the present approach the relevant matrix elements are very simple, as seen from eq. (7), and the iterative solution method, although often only useful for low eigenvalues, avoids explicit storage and manipulation of large matrices. All the $H(M, N)$ with $(M, N) \neq (M_0, N_0)$ are then adjusted according to the assignment

$$H(M,N) = W(M,N)\left[\alpha_x M + \alpha_y N + \alpha_x + \alpha_y - 2E\right]^{-1} \tag{9}$$

for some fixed $\alpha_x$, $\alpha_y$ and some trial $E$ value. In order to speed up the convergence of energy, we must choose appropriate initial values of convergence parameters. The energy is found from the relation (9) for the special case $M = M_0, N = N_0$, and the coefficient on the left-hand side becomes $H(M_0, N_0) = 1$. After this adjustment process a revised $E$ estimate $\underline{E}$ is calculated using the assignment statements

$$E_e = \left[2\alpha_x M + 2\alpha_y N + \alpha_x + \alpha_y\right] - W(M_0, N_0)\,, \tag{10}$$

$$\underline{E} = RE_e + (1 - R)E\,. \tag{11}$$

The relaxation parameter $R$ can be changed in value to help in stabilizing the convergence to a desired eigenvalue.

## 3. The recurrence relation for the potentials $V_3^m(x, y, z; \lambda, \eta, \mu, \xi)$ and $V_3^e(x, y, z; z_x^2, z_y^2, z_z^2, \lambda)$ in three dimensions

The algebraic manipulations needed to derive the required recurrence relation in three dimensions are similar to those which have been used previously in connection with the two-dimensional case.

To begin our analysis, we take the wavefunction describing this system in the form

$$\Psi_{n_x,n_y,n_z}(x,y,z) = \exp\left[-\tfrac{1}{2}\left(\alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2\right)\right] \sum H(M,N,L)\left(x^M y^N z^L\right). \tag{12}$$

If we use the wave function $\Psi_{n_x,n_y,n_z}(x, y, z)$ in the Schrödinger equation (1), after some algebra, we obtain the following recurrence relation for the potentials (3) and (4):

$$\left[2M\alpha_x + 2N\alpha_y + 2L\alpha_z + \alpha_x + \alpha_y + \alpha_z - E\right]H(M,N,L) = W(M,N,L)\,, \tag{13}$$

where, for the potential (3)

$$\begin{aligned} W(M,N,L) = {} & (M+2)(M+1)H(M+2,N,L) \\ & + (N+2)(N+1)H(M,N+2,L) \\ & + (L+2)(L+1)H(M,N,L+2) \\ & + (\alpha_x^2+\omega_x^2)H(M-2,N,L) + \left(\alpha_y^2+\omega_y^2\right)H(M,N-2,L) \\ & + (\alpha_z^2+\omega_z^2)H(M,N,L-2) \\ & - 2\lambda[H(M-1,N-2,L)+\eta H(M-3,N,L)] \\ & - 2\mu[H(M,N-1,L-2)+\xi H(M,N-3,L)] \end{aligned} \tag{14}$$

and for the potential (4)

$$\begin{aligned} W(M,N,L) = {} & (M+2)(M+1)H(M+2,N,L) \\ & + (N+2)(N+1)H(M,N+2,L) \\ & + (L+2)(L+1)H(M,N,L+2) \\ & + (\alpha_x^2+Z_x^2)H(M-2,N,L) + \left(\alpha_y^2+Z_y^2\right)H(M,N-2,L) \\ & + (\alpha_z^2+Z_z^2)H(M,N,L-2) \\ & - \lambda[H(M-4,N,L)+H(M,N-4,L)+H(M,N,L-4)] \\ & - 2\lambda[H(M-2,N-2,L)+H(M-2,N,L-2) \\ & + H(M,N-2,L-2)]\,. \end{aligned} \tag{15}$$

The initial condition to start the calculation is that $H(M_0, N_0, L_0) = 1$. All the $H(M, N, L)$ with $(M, N, L) \neq (M_0, N_0, L_0)$ are then calculated sequentially from the relation

$$H(M,N,L) = W(M,N,L)\left[2M\alpha_x + 2N\alpha_y + 2L\alpha_z + \alpha_x + \alpha_y + \alpha_z - E\right]^{-1}. \tag{16}$$

The energy estimate is revised using the relation (16) for the special case $M = M_0$, $N = N_0$, $L = L_0$. The coefficient on the left-hand side becomes $H(M_0, N_0, L_0) = 1$. The revised energy thus takes the form

$$E_e = 2M_0\alpha_x + 2N_0\alpha_y + 2L_0\alpha_z + \alpha_x + \alpha_y + \alpha_z - W(M_0,N_0,L_0) \tag{17}$$

or, with a relaxation parameter,

$$\underline{E} = RE_e + (1-R)E\,. \tag{18}$$

After many cycles the energy estimate coverges. The upper limits on $M$, $N$ and $L$ can then be increased and the calculation repeated, until eventually the energy is not affected by further increase in the upper limits. The upper limit in our calculation is $(M, N, L = Q = 60)$.

The convergence parameters $\alpha_x$, $\alpha_y$, $\alpha_z$ play an important role in controlling the convergence properties of our calculations. The optimum $\alpha_x$, $\alpha_y$, $\alpha_z$ values were initially obtained by numerical search, as illustrated by the data in Tables 5 and 6, which shows how varying the convergence parameters affects the accuracy of the energies obtained for the levels $E_{000}$, $E_{100}$ and $E_{111}$.

Table 1
Comparison of energy values for the potential $V_2(x, y; \lambda, \mu)$ with those from the exact quantum (EQ) [13], adiabatic approximation (AA) [11], semiclassical (SC) [13] and hypervirial (HR) [12] methods for several sets of perturbation parameters. The empty spaces mean the results are not available.

| $n_x$ | $n_y$ | Present result | EQ | AA | SC | HR |
|---|---|---|---|---|---|---|
| $\omega_x^2 = 0.29375, \omega_y^2 = 2.12581, \mu = 0.08414, \lambda = -0.1116$ | | | | | | |
| 0 | 0 | 0.9916262096827 | 0.9916 | 0.9918 | 0.9920 | 0.9918 |
| 1 | 0 | 1.5158523509194 | 1.5159 | 1.5170 | 1.5164 | 1.5170 |
| 0 | 1 | 2.4189087918281 | 2.4188 | 2.4194 | 2.4194 | 2.4194 |
| 1 | 1 | 2.9217575184111 | | | | |
| $\omega_x^2 = 0.36, \omega_y^2 = 1.96, \mu = 0.1, \lambda = -0.1$ | | | | | | |
| 0 | 0 | 0.9939049915996 | 0.9939 | 0.9940 | 0.9941 | 0.9940 |
| 1 | 0 | 1.5809044418757 | 1.5809 | 1.5815 | 1.5812 | 1.5815 |
| 0 | 1 | 2.3723335327149 | | | | |
| 1 | 1 | 2.9442568702125 | | | | |
| $\omega_x^2 = 0.49, \omega_y^2 = 1.69, \mu = 0.1, \lambda = -0.1$ | | | | | | |
| 0 | 0 | 0.9955188809798 | 0.9955 | 0.9956 | 0.9955 | 0.9956 |
| 1 | 0 | 1.6869942776770 | 1.6870 | 1.6873 | 1.6870 | 1.6873 |
| 0 | 1 | 2.2781315939504 | 2.2781 | 2.2783 | 2.2782 | 2.2783 |
| 1 | 1 | 2.9583526851367 | 2.9853 | 2.9593 | 2.9584 | 2.9593 |
| $\omega_x^2 = 0.81, \omega_y^2 = 1.21, \mu = 0.1, \lambda = -0.08$ | | | | | | |
| 0 | 0 | 0.9979600298595 | 0.9980 | 0.9980 | 0.9978 | 0.9980 |
| 1 | 0 | 1.8943550507194 | 1.8944 | 1.8947 | 1.8941 | 1.8947 |
| 0 | 1 | 2.0891226099777 | 2.0890 | 2.0894 | 2.0890 | 2.0894 |
| 1 | 1 | 2.9796174309586 | | | | |

## 4. Results and discussion

In this paper, we have improved the convergence properties of the Hill determinant approach by using the convergence factor $\exp[-\frac{1}{2}(\alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2)]$ for a three-dimensional system, in contrast to the previous work [8], which were limited to a uniform value of the convergence parameters ($\alpha_x = \alpha_y = \alpha_z$). The Hill determinant approach is revisited and implemented in a more effective way to give excellent accuracy even for potentials with mixed parity, whereas previous works [7,8] treated potentials with even parity only.

The numerical results for a two-dimensional system are presented in Tables 1 and 2, for the ground state and the first three excited states with different values of

Table 2
Comparison of energy values for potential $V_2(x, y; \lambda, \mu)$ with variation in perturbation parameters $\lambda$. $\omega_x^2 = 0.49, \omega_y^2 = 1.69, \lambda = -\mu$. The empty spaces mean the results are not available.

| $-\lambda$ | $n_x, n_y$ | Present result | EQ | AA | SC | HR |
|---|---|---|---|---|---|---|
| 0.06 | 0,0 | 0.99878298845122 | 0.9988 | 0.9988 | 0.9987 | 0.9988 |
| 0.08 | | 0.99750503091855 | 0.9975 | 0.9975 | 0.9975 | 0.9975 |
| 0.10 | | 0.99551888097989 | 0.9955 | 0.9956 | 0.9955 | 0.9956 |
| 0.12 | | 0.99259494493192 | 0.9926 | 0.9927 | 0.9927 | 0.9927 |
| 0.14 | | 0.988426091755 | 0.9884 | 0.9887 | 0.9889 | 0.9885 |
| 0.16 | | 0.98256799465 | 0.9826 | 0.9833 | 0.9836 | 0.9827 |
| 0.18 | | 0.9742855 | 0.9743 | 0.9761 | 0.9764 | 0.9745 |
| 0.20 | | 0.9619 | 0.9621 | 0.9668 | 0.9667 | 0.9625 |
| 0.06 | 1,0 | 1.69700382620682 | 1.6970 | 1.6971 | 1.6970 | 1.6971 |
| 0.08 | | 1.69330381519851 | 1.6933 | 1.6934 | 1.6933 | 1.6934 |
| 0.10 | | 1.68699427768 | 1.6870 | 1.6873 | 1.6870 | 1.6872 |
| 0.12 | | 1.6768856678 | 1.6769 | 1.6777 | 1.6770 | 1.6772 |
| 0.14 | | 1.66120482 | 1.6612 | 1.6634 | 1.6617 | 1.6616 |
| 0.16 | | 1.6369055 | 1.6370 | 1.6430 | 1.6382 | 1.6376 |
| 0.06 | 0,1 | 2.29318930861531 | 2.2932 | 2.2932 | 2.2932 | 2.2932 |
| 0.08 | | 2.28701021758891 | 2.2870 | 2.2871 | 2.2870 | 2.2871 |
| 0.10 | | 2.27813159395040 | 2.2781 | 2.2783 | 2.2782 | 2.2783 |
| 0.12 | | 2.265844300562 | 2.2658 | 2.2663 | 2.2661 | 2.2661 |
| 0.14 | | 2.249041496882 | 2.2490 | 2.2502 | 2.2496 | 2.2494 |
| 0.16 | | 2.2257015 | 2.2257 | 2.2288 | 2.2268 | 2.2263 |
| 0.06 | 1,1 | 2.98862233945227 | | | | |
| 0.08 | | 2.97681366046227 | | | | |
| 0.10 | | 2.95835268513667 | | | | |
| 0.12 | | 2.9305035186199 | | | | |
| 0.14 | | 2.88843544175 | | | | |
| 0.15 | | 2.859086 | | | | |
| 0.16 | | 2.82045 | | | | |

the perturbation parameters. It is clear that the Hill determinant approach works very well and gives results of high accuracy; we present a comparison of the Hill determinant results with those from the adiabatic approximation [13], hypervirial methods [14], exact quantum [15] and semiclassical [15] methods, for several sets of perturbation parameters $(\lambda, \omega_x^2, \omega_y^2, \mu)$.

In the three-dimensional case, we succeeded in finding energy values for the potential $V_3^m(x, y, z; \lambda, \eta, \mu, \xi)$ for several states with high accuracy for different values of the perturbation parameters. In Table 3, we compare our calculations with those calculated by another technique [18]. Again it is seen that the Hill determinant results give an accuracy higher than that of previous results [16,18].

It should be mentioned that the values of convergence parameters $\alpha_x$, $\alpha_y$, $\alpha_z$ which have been chosen to give the best convergence of eigenvalues in the present calculations for the potentials $V_2(x, y; \lambda, \mu)$ and $V_3^m(x, y, z, \lambda, \eta, \mu, \xi)$ were selected

Table 3
Energy levels for the potential $V_3^m(x, y, z; \lambda, \eta, \mu, \zeta)$ for several sets of perturbation. The results with underlines correspond to Noid et al. [18].

| $n_x$ | $n_y$ | $n_z$ | $-\lambda$ | $-\mu$ | $\eta$ | $\zeta$ | $\omega_x^2$ | $\omega_y^2$ | $\omega_z^2$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.49 | 1.69 | 1 |
| 0 | 0 | 0 | 1.493 752 135 656 4 | | | | | 1.494 | |
| 1 | 0 | 0 | 2.185 148 401 882 8 | | | | | 2.185 | |
| 0 | 1 | 0 | 2.771 863 548 529 0 | | | | | 2.771 | |
| 0 | 0 | 1 | 2.485 674 588 094 9 | | | | | 2.486 | |
| 1 | 0 | 1 | 3.176 716 038 054 7 | | | | | 3.177 | |
| 0 | 1 | 1 | 3.755 063 084 598 1 | | | | | | |
| $n_x$ | $n_y$ | $n_z$ | $-\lambda$ | $-\mu$ | $\eta$ | $\zeta$ | $\omega_x^2$ | $\omega_y^2$ | $\omega_z^2$ |
| | | | 0.1 | 0.1 | 0.1 | 0.1 | 1.44 | 1.69 | 1.21 |
| 0 | 0 | 0 | 1.797 312 142 821 8 | | | | | | |
| 1 | 0 | 0 | 2.994 932 205 133 7 | | | | | | |
| 0 | 1 | 0 | 3.088 731 039 392 4 | | | | | | |
| 0 | 0 | 1 | 2.890 761 654 017 6 | | | | | | |
| 1 | 0 | 1 | 4.087 785 982 444 0 | | | | | | |
| 0 | 1 | 1 | 4.176 686 910 250 4 | | | | | | |
| $n_x$ | $n_y$ | $n_z$ | $-\lambda$ | $-\mu$ | $\eta$ | $\zeta$ | $\omega_x^2$ | $\omega_y^2$ | $\omega_z^2$ |
| | | | 0.1 | 0.1 | 0.1 | 0.1 | 1 | 1 | 1 |
| 0 | 0 | 0 | 1.493 889 754 341 9 | | | | | | |
| 1 | 0 | 0 | 2.491 684 592 452 0 | | | | | | |
| 0 | 1 | 0 | 2.470 417 864 392 6 | | | | | | |
| 0 | 0 | 1 | 2.479 961 732 701 2 | | | | | | |
| 1 | 1 | 0 | 3.486 312 410 921 9 | | | | | | |
| 0 | 1 | 1 | 3.484 080 131 302 4 | | | | | | |

by looking for stability of the results with respect to the small variations of $\alpha_x$, $\alpha_y$, $\alpha_z$ at given values of the perturbation parameters; this picture is very clear in Table 5.

The energy eigenvalues for a double well potential $V_3^e(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ in a three-dimensional system are calculated, and their energy eigenvalues are given in Table 4, for several eigenstates $E_{000}$, $E_{010}$, $E_{001}$, $E_{011}$, $E_{110}$, $E_{101}$, $E_{111}$ and for various values of $Z_x^2$, $Z_y^2$, $Z_z^2$ and $\lambda$. We achieved results with high accuracy by varying the convergence parameters $\alpha_x$, $\alpha_y$, $\alpha_z$ and increasing the dimension of $H(M, N, L)$. Even higher accuracies can be achieved at the expense of greater computation times.

We should comment here that the sensitivity of the results for the double well potential $V_3^e(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ to the values of the convergence parameters is less

Table 4
Eigenvalues for the double-well potential $V_3^e(x, y, z; \lambda, Z_x^2, Z_y^2, Z_z^2)$ for several sets of parameters $\lambda$, $Z_x^2$, $Z_y^2$ and $Z_z^2$.

| $\lambda$ | $Z_x^2$ | $Z_y^2$ | $Z_y^2$ | (0, 0, 0) | (1, 0, 0) | (0, 1, 0) | (0, 0, 1) |
|---|---|---|---|---|---|---|---|
| 1.5 | 5 | 6 | 8 | −4.2089203909 | −1.2695363272 | −1.9487401637 | −3.8563290308 |
| 1 | 4 | 5 | 6 | −3.7951941464 | −1.4046920036 | −2.2457674270 | −3.3820801205 |
| 3 | 4 | 5 | 6 | 1.6920177798 | 5.4085248417 | 4.9428256619 | 4.4354816840 |
| 5 | 1 | 2 | 3 | 5.3813154487 | 10.8591103587 | 10.5317790363 | 10.1894331020 |
| 10 | 2 | 3 | 4 | 6.8694908083 | 13.6524250439 | 13.3915201768 | 13.1231886059 |
| 15 | 2.5 | 5 | 6 | 7.6288203735 | 15.4517096051 | 14.8773968036 | 14.6387792635 |
| 25 | 5 | 7.5 | 10 | 8.6400011334 | 17.6854676839 | 17.1955310426 | 16.6857992882 |
| 50 | 5 | 10 | 15 | 11.3959002985 | 23.1701253327 | 22.4075939324 | 21.6069719240 |
| $10^2$ | 10 | 20 | 30 | 13.4314180120 | 28.1489302777 | 26.9208539381 | 25.6133853735 |
| $10^3$ | 50 | 75 | 100 | 30.8470156963 | 62.0823088756 | 60.6648890561 | 59.1997061854 |
| $10^4$ | 100 | 150 | 200 | 75.4372892252 | 144.9710534466 | 143.7016756623 | 142.4142827569 |
| $10^5$ | 400 | 500 | 600 | 166.5007933768 | 316.5824930484 | 315.4196477084 | 314.2301591983 |
| $10^6$ | 500 | $10^3$ | $10^4$ | 342.8777073875 | 675.6813343918 | 673.0127649141 | 622.0165183266 |
| $\lambda$ | $Z_x^2$ | $Z_y^2$ | $Z_y^2$ | (0, 1, 1) | (1, 0, 1) | (1, 1, 0) | (1, 1, 1) |
| 1.5 | 5 | 6 | 8 | −0.9288022685 | −0.365963424 | 1.240162172 | 2.846361313 |
| 1 | 4 | 5 | 6 | −1.1538776288 | −0.469239288 | 0.472778214 | 2.057167192 |
| 3 | 4 | 5 | 6 | 8.5761831950 | 8.898034334 | 9.421983686 | 13.688715574 |
| 5 | 1 | 2 | 3 | 16.1671774815 | 16.463119215 | 16.772889953 | 23.045118524 |
| 10 | 2 | 3 | 4 | 20.6675488416 | 20.903648182 | 21.146591152 | 29.221425091 |
| 15 | 2.5 | 5 | 6 | 23.0878091383 | 23.606539393 | 23.822216095 | 32.944748459 |
| 25 | 5 | 7.5 | 10 | 26.6855508711 | 27.126820122 | 27.586277012 | 38.186366376 |
| 50 | 5 | 10 | 15 | 34.4194425131 | 35.108104259 | 35.831825933 | 49.223254109 |
| $10^2$ | 10 | 20 | 30 | 41.4570738270 | 42.560805592 | 43.738352405 | 60.047777705 |
| $10^3$ | 50 | 75 | 100 | 93.8487388021 | 95.128723987 | 96.452664870 | 133.383835350 |
| $10^4$ | 100 | 150 | 200 | 220.3512481378 | 221.507970413 | 222.680434249 | 307.057428627 |
| $10^5$ | 400 | 500 | 600 | 483.5899934131 | 484.659710800 | 485.735581406 | 670.408643046 |
| $10^6$ | 500 | $10^3$ | $10^4$ | 998.5727443619 | 1000.998437770 | 1047.399135131 | 1410.533240732 |

Table 5
The convergence of two eigenvalues for the states $\Psi_{000}$ and $\Psi_{100}$ for the potential $V_3^m(x, y, z; \lambda, \mu, \eta, \zeta)$, as a function of the convergence parameters $\alpha_x$, $\alpha_y$, $\alpha_z$. The empty spaces mean the eigenvalues cannot be obtained with the values of convergence parameters.

| $\lambda = 0.', \mu = -0.1, \eta = 0.1, \zeta = 0.1, \omega_x^2 = 0.49, \omega_y^2 = 1.69, \omega_z^2 = 1$ | | | |
|---|---|---|---|
| $E_{000}$ | $\alpha_x$ | $\alpha_y$ | $\alpha_z$ |
| | 0.6 | 0.7 | 0.8 |
| 1.4937521356564 | 0.98 | 0.96 | 1.1 |
| 1.4937521356564 | 1.1 | 1.2 | 1.3 |
| 1.4937521356 | 1.6 | 1.7 | 1.8 |
| 1.493752 | 2.2 | 2.4 | 2.6 |
| 1.494 | 2 | 2.5 | 2.8 |
| 1.49 | 2.5 | 2.8 | 3 |
| $E_{100}$ | $\alpha_x$ | $\alpha_y$ | $\alpha_z$ |
| | 0.6 | 0.7 | 0.8 |
| 2.18 | 0.95 | 0.98 | 1.1 |
| 2.1852 | 1.1 | 1 | 0.95 |
| 2.1851484018 | 1.2 | 1.15 | 1.1 |
| 2.1851484018828 | 1.4 | 1.1 | 1.2 |
| 2.1851484018828 | 1.5 | 1.2 | 1.25 |
| 2.18 | 1.7 | 1.6 | 1.8 |

Table 6
Convergence for some eigenvalues for the double-well potential $V_3^e(x, y, z; \lambda, Z_x^2, Z_y^2, Z_z^2)$ for several sets of parameters $\lambda$, $Z_x^2$, $Z_y^2$ and $Z_z^2$ for various values of the convergence parameters $\alpha_x$, $\alpha_y$, $\alpha_z$. The empty spaces mean the eigenvalues cannot be obtained with the values of convergence parameters.

| $\lambda$ | $Z_x^2$ | $Z_y^2$ | $Z_y^2$ | (0, 0, 0) | (1, 1, 1) | $\alpha_x$ | $\alpha_y$ | $\alpha_y$ |
|---|---|---|---|---|---|---|---|---|
| 15 | 2 | 4 | 6 | | | 4 | 5 | 6 |
| | | | | 7.8267987 | 33.378436 | 8 | 10 | 12 |
| | | | | 7.8267987280488 | 33.378436640432 | 10 | 12 | 14 |
| | | | | 7.8267987280488 | 33.378436640432 | 11 | 13 | 15 |
| | | | | 7.8267987 | 33.3784366 | 15 | 18 | 20 |
| $10^6$ | 500 | $10^3$ | $10^4$ | 342.8 | 1410.5 | 240 | 260 | 280 |
| | | | | 342.8777 | 1410.5332 | 300 | 320 | 340 |
| | | | | 342.877707387 | 1410.5332407 | 360 | 380 | 400 |
| | | | | 342.8777073875 | 1410.533240732 | 420 | 430 | 440 |
| | | | | 342.8777073875 | 1410.533240732 | 425 | 425 | 445 |
| | | | | 342.8777073875 | 1410.533240732 | 450 | 460 | 480 |

than in the case of the other potentials $V_2(x, y; \lambda, \mu)$ and $V_3^m(x, y, z; \lambda, \eta, \mu, \xi)$; this is clear from Table 6.

We should point out that Aitken's transformation applied to the iterates $E_n$ leads to an acceleration in the rate of convergence of the calculations and increases the accuracy for a given computing time.

## Acknowledgements

The author is grateful to the referees for their valuable comments and suggestions, in the light of which this paper has been revised. This research was supported in part by research grant No. GR/K17750 from EPSRC.

## References

[1] K.S.J. Nordholm and S.A. Rice, J. Chem. Phys. 61 (1974) 203.
[2] S.A. Rice, Adv. Chem. Phys. 47 (1981) 117.
[3] P. Brumer, Adv. Chem. Phys. 47 (1981) 201.
[4] G.D. Carney, L.L. Sprandel and C.W. Kern, Adv. Chem. Phys. 37 (1978) 305.
[5] L.L. Gibson, R.M. Roth, M.A. Ratner and R.B. Gerber, J. Phys. Chem. 85 (1986) 3425.
[6] D.W. Noid, M.L. Koszykowski and R.A. Marcus, Ann. Rev. Phys. Chem. 32 (1981) 267.
[7] M.R.M. Witwit, J. Comput. Phys. 123 (1996) 269; J. Math. Chem. 19 (1996) 75.
[8] J.P. Killingbeck, *Microcomputer Algorithms* (Hilger, Bristol, 1991); M.R.M. Witwit and J.P. Killingbeck, Can. J. Phys. 73 (1995) 632.
[9] D.W. Noid, M.L. Koszykowski, M. Tabor and R.A. Marcus, J. Chem. Phys. 72 (1980) 6169.
[10] R.A. Pullen and A.R. Edmonds, J. Phys. A: Math. Gen. 14 (1981) L319.
[11] Y. Weissman and J. Jortner, Chem. Phys. Lett. 78 (1981) 224.
[12] N. Pomphrey, J. Phys. B: Atom Molec. 7 (1974) 1909.
[13] Q. Zhi-Ding, Z. Xing-Guo, L. Xing-Wen, H. Kono and S.H. Lin, Molec. Phys. 47 (1982) 713.
[14] A. Requena, J. Zuniga, J.M. Frances and A. Hidalgo, Molec. Phys. 61 (1987) 1513.
[15] S. Chapman, B.C. Garrett and W.H. Miller, J. Chem. Phys. 64 (1976) 502.
[16] S.A. Meyer, M.A. Morgenstern, S.K. Kundson and D.W. Noid, Am. J. Phys. 59 (1991) 145.
[17] G.A. Arteca, F.M. Fernandez and E.A. Castro, Chem. Phys. Lett. 92 (1982) 43.
[18] D.W. Noid, M.L. Koszykowski and R.A. Marcus, J. Chem. Phys. 73 (1980) 391.
[19] S.K. Kundson and D.W. Noid, Chem. Phys. Lett. 145 (1988) 16.
[20] D.A. Estrin, F.M. Fernandez and E.A. Castro, J. Chem. Phys. 87 (1987) 7059.
[21] D.A. Estrin, F.M. Fernandez and E.A. Castro, J. Phys. A: Math. Gen. 23 (1990) 2395.