

Semiclassical energy levels for linear molecules Application to OCS

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Semiclassical energy levels and frequencies are obtained for the ground electronic state of OCS using the potential of Foord *et al.* [10]. Certain rotational corrections were neglected, as explained in the text. The frequencies typically differ from the calculated quantal values by about 0.2 cm^{-1} for the lower vibrational levels and about 2 cm^{-1} for the higher ones. Fifty levels were obtained using 145 s of CDC 7600 computing time.

1. INTRODUCTION

The same potential energy surfaces and the same dynamical equations control the interaction between three atoms in collision, such as $\text{O} + \text{CO} \rightarrow \text{O} + \text{CO}$ and when those same atoms are bound together to form a molecule such as CO_2 . Following the early calculations of Wall *et al.*, Blais and Bunker, Bunker and Karplus and Raff [1] classical trajectory methods have become an essential part of the theory of atom-molecule collisions. By contrast the application of classical and semiclassical theories to bound states of polyatomic molecules has yet to make its mark. There have been two impediments. One is that most spectroscopic observations in the past have been restricted to relatively small regions of potential energy surfaces, where the quantal calculations are feasible. The other is that the relationship between bounded classical motion and the observed spectra is more subtle than the relationship between classical trajectories and observed average cross sections.

Both these impediments have now been removed. The relationship between classical motion and spectra has been clarified with the recognition of the distinction between regular and irregular spectra and through the application of Einstein-Brillouin-Keller (EBK) quantization to the regular spectrum [2]. The use of lasers is extending the observed spectra into regions where standard quantal perturbation methods break down and the number of coupled vibrational states becomes so large that the matrix methods become clumsy or impractical. This includes the region of large quantum numbers where semiclassical theories are at their best. Semiclassical and quantal methods are complementary.

The classical analogue of the quantal bound state is the invariant toroid [2, 3, 4]. Semiclassical energy levels are the energies of those invariant toroids with quantized action integrals I_k (not to be confused with moments of inertia) of the form

$$I_k = \left(n_k + \frac{\alpha_k}{2} \right) \hbar \quad (1)$$

with integer n_k , where α_k is the Maslov index [2]. The problem is to obtain the invariant toroids and their action integrals. Analytic perturbation methods can be used close to equilibrium, as in quantum theory, but break down for high vibrational levels, as anharmonicities increase.

Three numerical methods have been used

- (M1) Stepwise integration of trajectories. This allows arbitrary distortion of the toroids, but estimation of the action integrals is difficult, particularly when the number of degrees of freedom increases beyond 2. It has been applied by Marcus and co-workers [5] and by Sorbie and Handy [6] to model systems of two degrees of freedom.
- (M2) Hamilton–Jacobi method. This does not allow arbitrary distortion of the toroids because of the awkward topological properties of the generating function of a canonical transformation. The associated singularities also affect convergence but the action integrals can easily be obtained. It is familiar as a numerical form of the theory presented by Born [7]. It has been applied by Handy *et al.* [8] to vibrational states of H_2O and SO_2 .
- (M3) Iteration–variation method [3, 4]. This makes use of a parametric representation of the toroid and allows arbitrary distortion, although large distortions are more difficult to handle than for (M1). The estimation of action integrals from the toroid is easy.

The experiments of Fayt and Vandenhoute [9] and the quantal calculations of Foord *et al.* (FSW, [10]) and Whiffen [11] on the ground electronic state of the OCS molecule are very suitable for comparison with semiclassical theory. The masses of all atoms are sufficiently large for the semiclassical approximation to be reliable and the anharmonicities are sufficiently great to provide an adequate test of the theory. However, OCS is linear and the consequent degeneracy of the bend modes requires a partial solution of the vibration–rotation problem. This paper gives a partial solution using the iteration–variation method (M3).

FSW use Hougen’s isomorphic hamiltonian expressed by Watson [12] in the form

$$H_{\text{iso}} = \frac{1}{2} \sum_k P_k^2 + \frac{\mu}{2} (\Pi_x'^2 + \Pi_y'^2) - \mu (\Pi_x' \pi_x + \Pi_y' \pi_y) + \frac{\mu}{2} (\pi_x^2 + \pi_y^2) + V(\mathbf{Q}). \quad (2)$$

They divided their quantal calculation into two parts. The first part was an ‘essential calculation’ which involved diagonalization of the vibrational hamiltonian

$$H_{\text{vib}} = \frac{1}{2} \sum_k P_k^2 + \frac{\mu}{2} (\pi_x^2 + \pi_y^2) + V(\mathbf{Q}) \quad (3)$$

using a harmonic oscillator basis set. The energy levels were tabulated for 69 values of the vibrational quantum numbers (v_1, v_2^l, v_3). The second part was concerned with perturbations due to the remaining terms of H_{iso} , giving rotational splitting as a function of the rotational quantum number J .

Our calculation is the semiclassical equivalent of FSW’s essential calculation, except that the term $(\mu/2)(\pi_x^2 + \pi_y^2)$ is included as a first-order perturbation on the remainder of H_{vib} . This is the precise semiclassical equivalent of the use of quantal first-order perturbation theory for $(\mu/2)(\pi_x^2 + \pi_y^2)$ using the eigenstates of the remainder. According to FSW this term does not contribute more than 5 cm^{-1} and the off-diagonal elements do not affect a transition by more than 0.15 cm^{-1} .

We do not attempt the second part of the calculation concerning the J quantum number. Only the essential calculation is carried out, because at this stage our purpose is to investigate the validity of semiclassical methods and is adequately fulfilled by comparing the results of the essential calculation using the same hamiltonian in semiclassical and quantum theories.

2. A SIMPLIFIED MODEL FOR THE BEND MODES

The vibration of a linear triatomic molecule such as OCS has two stretch modes and two degenerate orthogonal bend modes. If at first the coupling with the stretch modes is neglected, the bend modes have a hamiltonian of the form

$$H_2(x, y, p_x, p_y) = U(x^2 + y^2) + \frac{1}{2m} (p_x^2 + p_y^2), \quad (4)$$

where $U(z)$ is a smooth even function of z . This is identical in form to the hamiltonian of a particle moving in a smooth central potential in the (x, y) -plane with rotational symmetry, and it is in these simplified terms that we shall discuss the problem.

It is important in any calculation to reduce the effective number of degrees of freedom and to take advantage of any symmetries which enable one to do so. The simplified system (4) can clearly be solved by separating in polar coordinates (r, ϕ) but this introduces considerable difficulties if it is used for the original problem of the linear molecule. In both cases the separation produces a singular potential. For the simplified system this has the form L^2/r^2 , where L is the angular momentum, but the singularity has a much more complicated form for the original problem. Such singularities are to be avoided if possible for non-separable systems of more than one degree of freedom.

The iteration-variation method is described in papers I and II [4] to which the reader should refer. It is based on a parametric representation $\mathbf{X}(\theta)$ of a toroid in phase space. With this representation the effective number of degrees of freedom may be reduced without introducing new singularities. We show how this is done for the simplified system with hamiltonian (4).

A standard toroid for this system is two-dimensional; it depends on two angle variables θ_r and ϕ , say, which are conjugate to the action variables I_r and $L = I_\phi$. But the explicit dependence on ϕ can be removed. The angle variable ϕ represents a rotation of both the position (x, y) and momentum (p_x, p_y) . The hamiltonian is invariant under this rotation, resulting in conservation of the conjugate action variable L .

Because ϕ represents a rotation of the system, the toroid can always be expressed in the form

$$\mathbf{X}(\theta_r, \phi) = \mathcal{R}(\phi)\mathbf{Y}(\theta_r), \quad (5)$$

where $\mathbf{Y}(\theta_r)$ is a one-dimensional toroid (or closed trajectory) and $\mathcal{R}(\phi)$ is an operator that rotates both the position and momentum vectors of the phase point \mathbf{Y} through an angle ϕ .

We are left with the problem of obtaining the reduced toroid $\mathbf{Y}(\theta_r)$ which depends on only one angle variable instead of two. The number of dependent variables of the phase point \mathbf{Y} remains unchanged at four but the time of computation of \mathbf{Y} depends almost entirely on the number of angle variables, which determines the dimensionality of the arrays which appear.

The use of this representation for the toroid is equivalent to the use of a rotating frame, but unlike the usual classical rotating-frame methods we do not use the invariance under rotation to remove the angle of rotation from the hamiltonian, because this leads to the singular potentials that we wish to avoid.

3. VARIATIONAL PRINCIPLE AND ITERATION EQUATIONS

The angle hamiltonian equations are obtained from the variational principle for invariant toroids [3]. In using this variational principle we must obtain mean values over the angle variables. For the variable ϕ this is achieved by taking the mean over the rotations $\mathcal{R}(\phi)$.

For convenience we introduce the complex notation

$$\zeta = \frac{x + iy}{\sqrt{2}}, \quad \zeta^* = \frac{x - iy}{\sqrt{2}}, \quad (6 a)$$

$$p_\zeta = \frac{p_x - ip_y}{\sqrt{2}}, \quad p_\zeta^* = \frac{p_x + ip_y}{\sqrt{2}}, \quad (6 b)$$

so that the phase point is represented as

$$\mathbf{X} = (\zeta, \zeta^*, p_\zeta, p_\zeta^*). \quad (7)$$

The action variables are the action for radial motion

$$I_r = \left\langle p_\zeta \frac{\partial \zeta}{\partial \theta_r} + p_\zeta^* \frac{\partial \zeta^*}{\partial \theta_r} \right\rangle \quad (8)$$

and the angular momentum about the origin

$$L = i \langle \zeta p_\zeta - \zeta^* p_\zeta^* \rangle, \quad (9)$$

where the means $\langle \rangle$ are taken over θ_r .

The mean of the Hamiltonian over the toroid is

$$\langle H_2(\mathbf{X}) \rangle = \langle H_2(\mathbf{Y}) \rangle = \left\langle U(2\zeta\zeta^*) + \frac{1}{m} p_\zeta p_\zeta^* \right\rangle, \quad (10)$$

where the first equality follows from equation (5) and the invariance of the hamiltonian under rotation.

The functional

$$\Phi = \langle H_2(\mathbf{Y}) - \omega_r I_r - \omega_\phi L \rangle \quad (11)$$

is stationary with respect to variations in $\mathbf{Y}(\theta_r)$ subject to the action integrals remaining fixed [3]. ω_r and ω_ϕ are Lagrange multipliers which can be interpreted as frequencies for the radial and angular motion respectively.

To first order in the variations

$$0 = \Delta \Phi = \Delta \left\langle U(2\zeta\zeta^*) + \frac{1}{m} p_\zeta p_\zeta^* - \omega_r \left(p_\zeta \frac{\partial \zeta}{\partial \theta_r} + p_\zeta^* \frac{\partial \zeta^*}{\partial \theta_r} \right) - \omega_\phi i (\zeta p_\zeta - \zeta^* p_\zeta^*) \right\rangle. \quad (12)$$

If we neglect complex conjugates we obtain two independent equations

$$\left(\omega_r \frac{\partial}{\partial \theta_r} + i\omega_\phi \right) \zeta = \frac{1}{m} p_\zeta^*, \quad (13 a)$$

$$\left(\omega_r \frac{\partial}{\partial \theta_r} + i\omega_\phi \right) p_\zeta^* = - \frac{\partial U(2\zeta\zeta^*)}{\partial \zeta^*} \quad (13 b)$$

which may be combined to give the second-order 'newtonian' equation

$$\left(\omega_r \frac{\partial}{\partial \theta_r} + i\omega_\phi\right)^2 \zeta = -\frac{1}{m} \frac{\partial U(2\zeta\zeta^*)}{\partial \zeta^*}. \quad (14)$$

The last equation is used as a basis for an iteration scheme. The actual iteration of these equations is carried out for Fourier components ζ_s , where

$$\zeta(\theta_r) = \sum_{s=-\infty}^{\infty} \zeta_s \exp(is\theta_r) \quad (15)$$

and similarly for ζ^* , p_ζ and p_ζ^* .

We suppose that U is expressed as the sum of a harmonic and anharmonic term

$$U(2\zeta\zeta^*) = m\Omega^2 \zeta\zeta^* + U^{\text{anh}}(2\zeta\zeta^*) \quad (16)$$

and that F_ζ^{anh} is a force derived from the anharmonic part

$$F_\zeta^{\text{anh}}(2\zeta\zeta^*) = -\frac{\partial}{\partial \zeta^*} U^{\text{anh}}(2\zeta\zeta^*). \quad (17)$$

The iteration equation can therefore be written as

$$m[\Omega^2 - (s\omega_r + \omega_\phi)^2]\zeta_s = F_{\zeta_s}^{\text{anh}}. \quad (18)$$

Action integrals are related to frequencies and to Fourier components through the moment of inertia matrix equation [3].

$$\begin{pmatrix} L \\ I_r \end{pmatrix} = 2m \begin{pmatrix} \sum_{s=-\infty}^{\infty} |\zeta_s|^2 & \sum_{s=-\infty}^{\infty} s |\zeta_s|^2 \\ \sum_{s=-\infty}^{\infty} s |\zeta_s|^2 & \sum_{s=-\infty}^{\infty} s^2 |\zeta_s|^2 \end{pmatrix} \begin{pmatrix} \omega_\phi \\ \omega_r \end{pmatrix}, \quad (19)$$

Equation (19) leads to the following method of deriving the magnitudes $|\zeta_1|$ and $|\zeta_{-1}|$ of the fundamentals

$$|\zeta_{\pm 1}|^2 = \frac{1}{4m} \left| \frac{I_r' \pm L'}{\omega_r \pm \omega_\phi} \right|, \quad (20 a)$$

where

$$I_r' = I_r - 2m \sum_{\substack{s=-\infty \\ |s| \neq 1}}^{\infty} s(s\omega_r + \omega_\phi) |\zeta_s|^2, \quad (20 b)$$

$$L' = L - 2m \sum_{\substack{s=-\infty \\ |s| \neq 1}}^{\infty} (s\omega_r + \omega_\phi) |\zeta_s|^2. \quad (20 c)$$

The phases of ζ_1 and ζ_{-1} are obtained from the conditions $|x_1| = |y_1|$ and $\zeta_1 = \zeta_{-1}^*$ by using geometry in the complex plane. This gives $(1+i)/\sqrt{2}$ for the value of the phase factor of both ζ_1 and ζ_{-1} .

A semiclassical energy level $E_{v_2, l}^{\text{SC}}$ of the hamiltonian function (4) is given by the mean energy over the toroid with action integrals I_r , L which are quantized according to the rules

$$I_r = (v_2 + 1)\hbar, \quad (21 a)$$

$$L = l\hbar, \quad (21 b)$$

where v_2 and l are integers, the vibrational and rotational quantum numbers, which must satisfy the conditions

$$v_2 \geq 0, \quad |l| \leq v_2, \quad v_2 + l \text{ even.} \quad (21c)$$

The iteration procedure is similar to that of paper II except that a modified form of equation (18) is used for the iterations. We describe the modification for the simple model but it is also applied to the case of OCS in § 5. The modification is important in the neighbourhood of small divisors. It consists of rewriting equation (18) as

$$\zeta_s = \frac{(\Omega^2 - \omega_r^2)\zeta_s - F_{\xi_s}^{\text{anh}}/m}{[(s+1)\omega_r + \omega_\phi][(s-1)\omega_r + \omega_\phi]}. \quad (22)$$

For the computations the numerator of (22) is obtained from the Fourier integral of the function $(\Omega^2 - \omega_r^2)\zeta(\theta_r) - F_{\xi}^{\text{anh}}(\theta_r)/m$. If the denominator of (22) becomes very small we shall say that a small divisor has occurred.

4. A TEST OF THE THEORY

To test the theory and method outlined in the previous section the iteration procedure was applied to hamiltonian (4) with

$$U(x^2 + y^2) = \frac{m}{2} \Omega_2^2 (x^2 + y^2) + k_{2222} (x^2 + y^2)^2. \quad (23)$$

When expressed in terms of the complex coordinates with which the theory was developed, the hamiltonian is

$$H_2 = \frac{1}{m} p_\zeta p_\zeta^* + m \Omega_2^2 \zeta \zeta^* + 4k_{2222} (\zeta \zeta^*)^2. \quad (24)$$

Choosing $\Omega_2 = 523.62$, $k_{2222} = 1.77\Omega_2^2$ and units such that $\hbar = m = 1$, semiclassical energy levels $E_{v_2, l}^{\text{SC}}$ for selected values of v_2 and l were calculated using iteration equations (22), (19) and (20). These energy levels are presented in table 1 and were obtained without difficulty.

If we express (24) in terms of polar coordinates (r, ϕ) where $r^2 = 2\zeta \zeta^*$, the hamiltonian becomes

$$H_2 = \frac{1}{2m} \left(p_r^2 + \frac{p_\phi^2}{r^2} \right) + \frac{m}{2} \Omega_2^2 r^2 + k_{2222} r^4. \quad (25)$$

This hamiltonian is of course separable, so we can write

$$p_\phi = \text{constant (angular momentum)} = l \quad (26)$$

and obtain the one-dimensional hamiltonian with l^2/r^2 singularity

$$H_2 = \frac{1}{2m} p_r^2 + \frac{m}{2} \Omega_2^2 r^2 + \frac{l^2}{2mr^2} + k_{2222} r^4. \quad (27)$$

As mentioned in the introduction, the singularity is precisely what we have sought to avoid with the new theory. However, the calculation of semiclassical energy levels $E_{n, l}^{\text{SC}}$ of (27) provides a convenient check for the theory, since energy levels furnished by the two methods must have identical values.

Table 1. Semiclassical energy levels for a model hamiltonian representing the uncoupled bend modes of OCS.

$$H_2 = \frac{1}{m} p_\zeta p_\zeta^* + m \Omega_2^2 \zeta \zeta^* + 4k_{2222}(\zeta \zeta^*)^2,$$

$$\Omega_2 = 523.62 \text{ cm}^{-1},$$

$$k_{2222} = 1.77 \Omega_2^2 \text{ cm}^{-3}.$$

$$\hbar = m = 1$$

Level (v_2, l)	Energy E^{SC} cm^{-1}	Anharmonicity $\Delta E^{\text{anh}\dagger}$ cm^{-1}
00	526.25	2.63
11	1056.80	9.56
22	1590.72	19.85
20	1594.10	23.24
33	2127.92	33.44
31	2134.61	40.13

$\dagger \Delta E^{\text{anh}}$ are the energies by which the semiclassical levels are exceeded by the values they would have if the anharmonic force was neglected.

Energy levels of (27) were calculated using the standard techniques of paper II for non-degenerate hamiltonians. The quantized action integral for this one-dimensional problem is defined by

$$I = (n + \frac{1}{2})\hbar, \quad (28 a)$$

where

$$n = (v_2 - l)/2. \quad (28 b)$$

For the one-dimensional problem it proved to be difficult to obtain convergence because of the singularity. It was necessary to increase I by small increments from zero to its quantized value defined by equation (28). In this way it was eventually possible to reproduce identically the values $E_{v_2, l}^{\text{SC}}$ obtained by the new method. The superiority of the new method was amply demonstrated for this simplified case.

5. APPLICATION TO OCS

The potential energy function for a linear triatomic molecule such as OCS has the form

$$V(\mathbf{Q}) = \frac{1}{2} \sum_{i=1}^3 \Omega_i^2 Q_i^2 + \sum'_{i,j,k} k_{ijk} Q_i Q_j Q_k + \sum'_{i,j,k,l} k_{ijkl} Q_i Q_j Q_k Q_l + \dots, \quad (29)$$

where the prime indicates the restricted summation $i \leq j \leq k$ [10]. Normal coordinates Q_1 and Q_3 refer to symmetric and asymmetric stretching vibrations, respectively, while Q_2 is the (degenerate) bending coordinate. $V(\mathbf{Q})$ is an even function of Q_2 . Ω_1, Ω_2 and Ω_3 are the equilibrium classical vibrational frequencies

For their quantal calculations, FSW include all terms in the potential energy up to fourth order, and also retain the quintic term $k_{22223} Q_2^4 Q_3$ to

adequately represent effects due to the near equality of $4\Omega_2$ and Ω_3 and the resulting Fermi resonance. The potential constants appear in table 2. We use Watson's normal coordinates instead of those of FSW, consequently the k coefficients appearing in table 2 differ from those in [10] by a frequency factor.

Table 2. Constants for $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ hamiltonian.

Constant	Value
$\Omega_1/(\text{c cm}^{-1})$	875.70
$\Omega_2/(\text{c cm}^{-1})$	523.62
$\Omega_3/(\text{c cm}^{-1})$	2092.46
$k_{111}/\Omega_1^{3/2} \text{ cm}^{-1}$	-33.59
$k_{113}/\Omega_1\Omega_3^{1/2} \text{ cm}^{-1}$	53.52
$k_{122}/\Omega_1^{1/2} \Omega_2 \text{ cm}^{-1}$	42.95
$k_{133}/\Omega_1^{1/2} \Omega_3 \text{ cm}^{-1}$	-125.24
$k_{223}/\Omega_2\Omega_3^{1/2} \text{ cm}^{-1}$	51.30
$k_{333}/\Omega_3^{3/2} \text{ cm}^{-1}$	-67.01
$k_{1111}/\Omega_1^2 \text{ cm}^{-1}$	1.55
$k_{1113}/\Omega_1^{3/2} \Omega_3^{1/2} \text{ cm}^{-1}$	-4.40
$k_{1122}/\Omega_1\Omega_2 \text{ cm}^{-1}$	-4.95
$k_{1133}/\Omega_1\Omega_3 \text{ cm}^{-1}$	6.40
$k_{1223}/\Omega_1^{1/2} \Omega_2\Omega_3^{1/2} \text{ cm}^{-1}$	-2.38
$k_{1333}/\Omega_1^{1/2} \Omega_3^{3/2} \text{ cm}^{-1}$	0.84
$k_{2222}/\Omega_2^2 \text{ cm}^{-1}$	1.77
$k_{2233}/\Omega_2\Omega_3 \text{ cm}^{-1}$	-19.28
$k_{3333}/\Omega_3^2 \text{ cm}^{-1}$	3.98
$k_{22223}/\Omega_2^2 \Omega_3^{1/2} \text{ cm}^{-1}$	-0.45
$I^0/(\text{u } \text{Å})$	82.96
$a_1/\text{u}^{1/2} \text{ Å}$	17.90
$a_3/\text{u}^{1/2} \text{ Å}$	3.31
ζ_{12}	-0.1815
ζ_{23}	0.9833

The kinetic energy function for OCS for the essential calculation has the form

$$T = \frac{1}{2} \sum_{i=1}^3 P_i^2 + \frac{\mu}{2} (\pi_x^2 + \pi_y^2). \quad (30)$$

P_i are momenta conjugate to Q_i and $(\mu/2)(\pi_x^2 + \pi_y^2)$ can be written as

$$\frac{\mu}{2} (\pi_x^2 + \pi_y^2) = \frac{\mu}{2} [\zeta_{12}(Q_1P_2 - Q_2P_1) + \zeta_{23}(Q_2P_3 - Q_3P_2)]^2, \quad (31 a)$$

where

$$\mu = I^0 / (I^0 + \frac{1}{2}a_1Q_1 + \frac{1}{2}a_3Q_3)^2. \quad (31 b)$$

I^0 is the moment of inertia for OCS in its linear equilibrium configuration and ζ_{12} and ζ_{23} are Coriolis coupling coefficients. Values for the constants appearing in equation (31) are given in table 2.

Since the contribution to the total energy of the term $(\mu/2)(\pi_x^2 + \pi_y^2)$ is small ($\approx 5 \text{ cm}^{-1}$ for the higher levels computed [10]) compared with the anharmonicity introduced by $V(\mathbf{Q})$ (typically 100 cm^{-1} for the higher levels), it is a good approximation to consider $(\mu/2)(\pi_x^2 + \pi_y^2)$ as a perturbation on the hamiltonian

$$H = \frac{1}{2} \sum_{i=1}^3 P_i^2 + V(\mathbf{Q}) \quad (32)$$

with $V(\mathbf{Q})$ given by (29).

Incorporation of the theory and method of § 3 into a scheme for calculating semiclassical energy levels of (32) is straightforward. Here we write only the iteration equations for the Fourier components of the toroid :

Bend :

$$\zeta_s = \frac{(\Omega_2^2 - \omega_r^2)\zeta_s - F_{\zeta_s}^{\text{anh}}}{[s_1\omega_1 + (s_2 + 1)\omega_r + s_3\omega_3 + \omega_\phi][s_1\omega_1 + (s_2 - 1)\omega_r + s_3\omega_3 + \omega_\phi]}, \quad (33 a)$$

$$Q_{1s} = \frac{(\Omega_1^2 - \omega_1^2)Q_{1s} - F_{Q_{1s}}^{\text{anh}}}{[(s_1 + 1)\omega_1 + s_2\omega_r + s_3\omega_3][(s_1 - 1)\omega_1 + s_2\omega_r + s_3\omega_3]}, \quad (33 b)$$

Stretch :

$$Q_{3s} = \frac{(\Omega_3^2 - \omega_3^2)Q_{3s} - F_{Q_{3s}}^{\text{anh}}}{[s_1\omega_1 + s_2\omega_r + (s_3 + 1)\omega_3][s_1\omega_1 + s_2\omega_r + (s_3 - 1)\omega_3]}, \quad (33 c)$$

where

$$\mathbf{s} = (s_1, s_2, s_3), \quad (34 a)$$

$$Q_2^2 = 2\zeta\zeta^* \quad (34 b)$$

and

$$F_{Q_k}^{\text{anh}} = -\frac{\partial V^{\text{anh}}}{\partial Q_k}. \quad (34 c)$$

(N.B. The complex coordinate ζ and Fourier components ζ_s should not be confused with the Coriolis coupling coefficients ζ_{12} and ζ_{23} .)

A quantal energy level of (32) is labelled by four quantum numbers (v_1, v_2, v_3) . These are related to four classical action integrals by the following semiclassical quantization rules :

$$I_1 = (v_1 + \frac{1}{2})\hbar, \quad (35 a)$$

$$I_r = (v_2 + 1)\hbar, \quad (35 b)$$

$$L = \hbar \quad (35 c)$$

$$I_3 = (v_3 + \frac{1}{2})\hbar. \quad (35 d)$$

After calculating each desired toroid and energy E of equation (32) the precise semiclassical equivalent of quantal first-order perturbation theory is used to determine the contribution to the total energy of the term $(\mu/2)(\pi_x^2 + \pi_y^2)$. This simply involves the calculation of

$$E^{\text{pert}} = \left\langle \frac{\mu}{2} (\pi_x^2 + \pi_y^2) \right\rangle, \quad (36)$$

where $\langle \rangle$ denotes a mean over the calculated toroid. The energy E^{pert} is added to E and each sum is compared with the corresponding quantal energy level calculated by FSW to give a direct evaluation of the precise of semi-classical (EBK) quantization. This evaluation is subject to an error of no more than 0.2 cm^{-1} in the energy of the classical toroids and to any errors there might be in the quantal calculation.

6. COMPUTATION METHOD

A reduced toroid (§ 2) for the linear OCS molecule depends on three angle variables. Each triply periodic function $f_3(\theta_1, \theta_r, \theta_3)$ is approximated by a finite Fourier sum of $N_1 \times N_2 \times N_3$ terms. The functions f_3 are tabulated on an $N_1 \times N_2 \times N_3$ mesh of equally spaced points spanning the space of the angle variables $-\pi < \theta_1 \leq \pi$, $-\pi < \theta_r \leq \pi$, $-\pi < \theta_3 \leq \pi$. Mean values are calculated from tabulated meshes.

The presence of small divisors can affect convergence of the iteration procedure. A small divisor occurs whenever calculated frequencies approximately satisfy a low-order resonance condition such as a Fermi resonance. If a small divisor appears during the iterations for a toroid, the Fourier components associated with that divisor become large. As a consequence the new fundamentals calculated from the moment of inertia matrix equation become artificially small. Since frequencies are calculated from fundamentals, small divisors lead to fluctuations in the frequencies which affect all Fourier components of the toroid at the next stage of the iteration.

Energy levels are calculated from converged toroids with quantized action integral. An invariant toroid can only be considered to have converged if from one iteration to the next no Fourier component of the toroid changes by more than a chosen tolerable amount. Associated with each energy level and corresponding converged toroid is a set of frequencies which may satisfy a low-order resonance condition. If this is the case, the iteration procedure may never produce the desired converged toroid or the correct semiclassical energy.

Clearly there are too many Fourier components to test individually. Instead we choose to test for convergence of the energy, at the same time checking for fluctuations in the frequencies and fundamentals which would indicate the influence of small divisors. First a crude convergence criterion TOL1 say, is chosen and the iterations carried out, retaining only the fundamentals and constant terms of the Fourier series until the difference between successive values of the mean energy is less than TOL1. For this stage no small divisors can be encountered. When convergence to TOL1 has been achieved N_1 , N_2 and N_3 are increased, typically to eight, and the iterations proceed until the difference between successive mean energies is less than a new tolerable value $\text{TOL2} < \text{TOL1}$. If there are no important small divisors then TOL2 will determine the accuracy of the semiclassical energy. A further increase of the N_i is required to leave the energy unchanged to within TOL2.

To obtain an energy spectrum the invariant toroid for one energy level is used as a starting-point for the iterations for the next level. Further details can be found in paper II.

The computer program was tested by separately uncoupling each vibrational mode from the remainder. Energy levels were calculated for the resulting

partially separated systems and compared with levels produced using a combination of well-tested programs [4] and the method of § 4 for treating the angular momentum.

For the computations using the empirical OCS potential of Foord *et al.* reported in the following section, $TOL1=1.5 \text{ cm}^{-1}$ and $TOL2=0.1 \text{ cm}^{-1}$ were chosen as convergence criteria for the levels and $N_1=N_2=N_3=8$ defined the final length of the Fourier series. Additional checks on the convergence of certain levels were made by further increasing N_1 or N_2 or N_3 to 16. Visual checks were made on every level to ensure that calculated frequencies and fundamentals were well behaved.

7. RESULTS AND DISCUSSION

Table 3 presents the semiclassical energy levels of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ calculated by the methods described in §§ 5 and 6, and using the empirical potential of FSW [10]. An attempt was made to obtain all the energy levels of [10], but the iteration procedure did not always converge, and the level is then denoted by a — in the table. The tolerances allowed are given in § 6. The computation of the 50 converged levels took 145 s on a CDC 7600 computer.

Table 3. Comparison of semiclassical and quantal energy levels for the ground electronic state of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$.

1			2	3	4	5	6
Level			$E^{\text{SC}} (a)$	$\Delta E (b)$	$\nu^{\text{SC}} (c)$	$\Delta \nu (d)$	$\Delta \nu^{\text{anh}} (e)$
v_1	v_2^l	v_3	cm^{-1}	(ΔE) cm^{-1}	cm^{-1}	$(\Delta \nu)$ cm^{-1}	cm^{-1}
0	0 ⁰	0	1998.1	1.3 (1.3)	0	0 (0)	0
1	0 ⁰	0	2857.4	1.0 (1.1)	859.3	-0.3 (-0.2)	16.7
0	2 ⁰	0	3044.9	1.5 (1.5)	1046.8	0.2 (0.2)	0.2
2	0 ⁰	0	3708.7	1.3 (1.3)	1710.6	0.0 (0.0)	40.8
1	2 ⁰	0	3889.9	1.6 (1.6)	1891.8	0.3 (0.3)	30.8
0	0 ⁰	1	4060.0	1.4 (1.3)	2061.9	0.1 (0.0)	30.4
0	4 ⁰	0	4103.3	2.2 (2.1)	2105.2	0.9 (0.8)	-11.7
3	0 ⁰	0	4552.9	1.6 (1.4)	2554.8	0.3 (0.1)	72.1
2	2 ⁰	0	—	—	—	—	67.9
1	0 ⁰	1	4916.5	1.0 (0.9)	2918.4	-0.3 (-0.4)	50.1
1	4 ⁰	0	4933.3	2.5 (2.1)	2935.2	1.2 (0.8)	33.8
0	2 ⁰	1	5093.2	1.4 (1.1)	3095.1	0.1 (-0.2)	44.5
0	6 ⁰	0	5172.1	4.0 (3.0)	3174.0	2.7 (1.7)	-34.9

Table 3 (continued)

1			2	3	4	5	6
Level			$E^{\text{SC}}(a)$	$\Delta E(b)$	$\nu^{\text{SC}}(c)$	$\Delta \nu(d)$	$\Delta \nu_{\text{anh}}(e)$
v_1	v_2^l	v_3	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
4	0 ⁰	0	5390.0	4.6 (1.0)	3391.9	3.3 (-0.3)	107.7
3	2 ⁰	0	—	—	—	—	110.6
2	4 ⁰	0	—	—	—	—	83.3
2	0 ⁰	1	5765.9	1.5	3767.8	0.2	75.8
1	2 ⁰	1	—	—	—	—	77.7
1	6 ⁰	0	—	—	—	—	17.2
0	0 ⁰	2	6102.2	-1.0	4104.1	-2.3	83.5
0	4 ⁰	1	6139.3	1.9	4141.2	0.6	45.1
3	0 ⁰	1	6607.2	2.5	4609.1	1.2	109.4
2	2 ⁰	1	—	—	—	—	117.4
1	0 ⁰	2	6956.5	-2.7	4958.4	-4.0	106.2
1	4 ⁰	1	—	—	—	—	91.1
0	1 ¹	0	2518.4	1.4 (1.4)	520.3	0.1 (0.1)	3.3
1	1 ¹	0	3370.8	1.4 (1.2)	1372.7	0.1 (-0.1)	26.5
0	3 ¹	0	3571.3	1.7 (1.4)	1573.2	0.4 (0.1)	-2.8
2	1 ¹	0	—	—	—	—	56.8
1	3 ¹	0	4409.3	1.7 (1.3)	2411.2	0.4 (0.0)	35.0
0	1 ¹	1	4573.5	1.1 (0.7)	2575.4	-0.2 (-0.6)	40.9
0	5 ¹	0	4635.0	2.7 (2.3)	2636.9	1.4 (1.0)	-20.2
3	1 ¹	0	5055.1	1.4 (0.9)	3057.0	0.1 (-0.4)	93.7
2	3 ¹	0	—	—	—	—	78.8
1	1 ¹	1	—	—	—	—	67.2
1	5 ¹	0	5457.8	2.5 (1.6)	3459.7	1.2 (0.3)	32.9
0	3 ¹	1	5613.1	1.5	3615.0	0.2	48.1
0	7 ¹	0	5709.5	4.3	3711.4	3.0	-49.0
4	1 ¹	0	5887.1	3.5	3889.0	2.2	135.2
3	3 ¹	0	—	—	—	—	127.5
2	1 ¹	1	—	—	—	—	100.6
2	5 ¹	0	—	—	—	—	86.8
1	3 ¹	1	6448.7	1.6	4450.6	0.3	88.1
1	7 ¹	0	—	—	—	—	9.2
0	1 ¹	2	6604.1	1.5	4606.0	0.2	102.3
0	5 ¹	1	6665.5	2.0	4667.4	0.7	42.4
3	1 ¹	1	7102.1	3.3	5104.0	2.0	137.2

Table 3 (continued)

1			2	3	4	5	6
Level			$E^{\text{SC}} (a)$	$\Delta E (b)$	$\nu^{\text{SC}} (c)$	$\Delta \nu (d)$	$\Delta \nu^{\text{anh}} (e)$
v_1	v_2^l	v_3	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
2	3 ¹	1	7279.3	0.8	5281.2	-0.5	134.1
1	1 ¹	2	—	—	—	—	131.7
0	2 ²	0	3038.9	1.4 (0.6)	1040.8	0.1 (-0.7)	6.3
1	2 ²	0	3884.8	1.5 (0.7)	1886.7	0.2 (-0.6)	36.0
0	4 ²	0	4097.5	2.0 (1.1)	2099.4	0.7 (-0.2)	-5.6
2	2 ²	0	—	—	—	—	72.3
1	4 ²	0	4928.4	2.0 (1.0)	2930.3	0.7 (-0.3)	39.2
0	2 ²	1	5086.9	1.3 (0.3)	3088.8	0 (-1.0)	50.9
0	6 ²	0	5166.6	2.8 (1.8)	3168.5	1.5 (0.5)	-28.5
3	2 ²	0	—	—	—	—	114.7
2	4 ²	0	5753.8	1.8	3755.7	0.5	89.6
1	2 ²	1	5929.3	1.9	3931.2	0.6	83.6
1	6 ²	0	5981.2	3.5	3983.1	2.2	32.2
0	4 ²	1	6133.2	1.5	4135.1	0.2	51.6
0	8 ²	0	—	—	—	—	-62.8
4	2 ²	0	6386.6	0.8	4388.5	-0.5	162.1
3	4 ²	0	—	—	—	—	144.2
0	3 ³	0	3559.6	1.4 (3.1)	1561.5	0.1 (1.8)	9.3
1	3 ³	0	4399.3	1.4 (0.5)	2401.2	0.1 (-0.8)	45.3
0	5 ³	0	4623.8	2.1 (0.0)	2625.7	0.8 (-1.3)	-8.4
2	3 ³	0	5232.4	1.9 (-0.1)	3234.3	0.6 (-1.4)	87.4
1	5 ³	0	5447.7	2.1 (-0.1)	3449.6	0.8 (-1.4)	43.4

(a) Semiclassical energy levels for $N_1=N_2=N_3=8$, $\text{TOL2}=0.1 \text{ cm}^{-1}$.

(b) $\Delta E = E^{\text{Q}} - E^{\text{SC}}$, where E^{Q} is the quantal energy of FSW [10]. Bracketed values are from Whiffen [11]. The illustrated FSW values and the semiclassical values follow the convention of omitting all π' terms. The Whiffen [11] results follow a different convention, in which $-B_e l^2$ is included. For comparison add approximately $0.2l^2 \text{ cm}^{-1}$ to the bracketed values.

(c) $\nu^{\text{SC}} = E^{\text{SC}} - (0\ 0\ 0)^{\text{SC}}$ are energy differences from ground vibrational level.

(d) $\Delta \nu = \nu^{\text{Q}} - \nu^{\text{SC}}$ where ν^{Q} is the quantal energy difference from the ground vibrational level [10]. Bracketed values are from Whiffen [11].

(e) $\Delta \nu^{\text{anh}}$ are the energies by which the quantal levels are exceeded by the values that they would have if anharmonic forces were neglected. The value for $(0\ 0\ 0)$ is subtracted from the entire column.

Lack of convergence was always due to the presence of small divisors, where the denominator on the right-hand side of equation (33) became very small. This problem is not confined to the method used here but arises from an intrinsic property of the invariant toroids, recognized by Poincaré in his treatment of celestial mechanics and related to Fermi resonances in molecules. There are methods for overcoming this difficulty provided the spectrum remains regular as defined in [2], but a discussion of these methods would go beyond the scope of this paper.

In table 3, column 2 contains the semiclassical energy levels and column 3 the energy by which these levels are exceeded by the corresponding quantal levels obtained by FSW [10] and by Whiffen [11] in an improved quantal calculation using the same potential. In column 4 the semiclassical energy of the ground level (0 0⁰ 0) is subtracted from column 2, giving energy differences which are proportional to observable frequencies, and in column 5 appear the energies by which these are exceeded by the corresponding quantal values.

The final column 6 contains the energies by which the quantal levels are exceeded by the values that they would have if anharmonic forces were neglected. The value for (0 0⁰ 0) is subtracted from the entire column.

Comparison of columns 3, 5 and 6 provides a measure of the errors.

Handy *et al.* [8] have applied the Hamilton–Jacobi method (M2) to obtain five low-lying vibrational energy levels of SO₂ and H₂O which they compare with corresponding quantal values. For SO₂ the semiclassical and quantal energy differences from the ground level agree to better than 0.1 cm⁻¹. For H₂O, which exhibits stronger anharmonicities, agreement is to about 1.5 cm⁻¹ for the worst case. This is comparable to the calculated difference for OCS. It is expected that the character of the molecular potential and not the difference in method accounts for the excellent agreement for SO₂.

The iteration–variation method described in this paper is fast, and obtains the main features of the observable spectrum of a linear triatomic molecule, but the precision, as measured by the difference between quantal and semiclassical energy levels, does not approach that of modern spectroscopy. The errors are either due to the inadequacy of the lowest order semiclassical approximation, or to errors discussed at the end of § 5.

The necessity of taking special account of the presence of small divisors when calculating the toroids is apparent, and also possibly when obtaining corrections of higher order in \hbar .

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