

# Energies and widths of quasibound levels (orbiting resonances) for spherical potentials<sup>a)</sup>

Robert J. Le Roy and Wing-Ki Liu

Guelph-Waterloo Center for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 27 April 1978)

Various methods for calculating the energies and widths of quasibound levels (orbiting or shape resonances) for spherical potentials are critically compared. A derivation for the previously-proposed Airy function boundary condition method is presented, and a Weber function boundary condition method for locating resonances which lie above the potential barrier maximum is derived, tested, and found wanting. It is shown that the Weyl  $m$ -function method of Hehenberger *et al.* [J. Chem. Phys. **65**, 4559 (1976)] yields results in essentially exact agreement with the time-delay maximum method of Le Roy and Bernstein [J. Chem. Phys. **54**, 5114 (1971)]. An improved semiclassical method of calculating these resonance widths, suggested by Child, is presented and shown to be reliable even for levels lying right at a potential barrier maximum.

## I. INTRODUCTION

At energies above the asymptote of a spherical potential function there exists a continuum of allowed radial eigenstates. If the effective potential curve has a positive maximum of the type shown in Fig. 1, the eigenfunctions over the potential well (in the region  $a < R < b$ ) at most energies between the potential asymptote and barrier maximum have very small amplitudes, so that the system is effectively excluded from this region of space.<sup>1</sup> However, in narrow energy intervals whose positions approximately correspond to the eigenvalues this potential curve would have if its asymptote was at the barrier maximum energy  $V_{\max}$ , the continuum wavefunctions over the well have relatively large amplitudes, and the system behaves somewhat as if it were in a bound state. These energy intervals correspond to the quasibound level or orbiting resonance states of the system. Their considerable influence on physical and chemical phenomena has stimulated numerous studies on their properties, an excellent review of which has been presented by Child.<sup>2</sup> The present paper critically examines a number of methods for calculating the position and widths of these resonances and attempts to determine the most accurate and efficient way of doing this.

Orbiting resonances may be described theoretically using a variety of properties of the wave functions. In particular, the collisional time delay<sup>3-5</sup> and the internal amplitude function<sup>5-9</sup> characterize resonance features of the wavefunctions at real energies, while the Siegert pole formalism<sup>2,10</sup> and the Weyl-Titchmarsh  $m$  function<sup>11-13</sup> are associated with analytic continuation of the wavefunction to complex energies. While each of these approaches defines a "unique" resonance position and width, it is difficult to ascertain which is more fundamentally related to physically observable resonance phenomena. For very narrow resonances, the various methods for calculating these quantities are in essentially exact agreement. However, for broad quasibound

levels<sup>14</sup> lying near or above a potential barrier maximum, their predictions often differ by a significant fraction of the level width  $\Gamma$  (e.g., by  $\sim 0.05\Gamma$  for the position and up to  $0.3\Gamma$  for the width<sup>5,11-13</sup>). At the same time, a unique resonance energy is an almost impossible quantity to determine experimentally. Bernstein *et al.*<sup>15</sup> showed that the resonance structure in a scattering cross section can exhibit a variety of shapes, no single feature of which defines the resonance position uniquely. Moreover, different "discrete" spectroscopic transitions into a given quasibound level may suggest slightly different positions because of differences in the energy dependence of the corresponding Franck-Condon overlap integrals. As a result, it appears that for broad resonances,<sup>14</sup> discrepancies in the predicted positions and widths of  $\sim 0.05\Gamma$  and  $0.1-0.3\Gamma$ , respectively, are effectively negligible, in that there is no basis, experimental or theoretical, for choosing between them.

As mentioned above, there exist a number of "exact" quantum-mechanical methods which define the resonance positions and widths in terms of the characteristic behavior of properties of the exact radial wavefunctions. Unfortunately, use of these methods is relatively tedious, both because the wavefunction must be numerically integrated into the asymptotic region where the noncentrifugal part of the potential is negligible, and because there is no efficient algorithm for rapidly converging on a resonance energy. In view of these difficulties, a number of approximate "boundary condition" techniques for locating resonances were proposed.<sup>5,8,16,17</sup> In these methods, the wavefunction is required to have some chosen behavior at a selected outer boundary. Com-

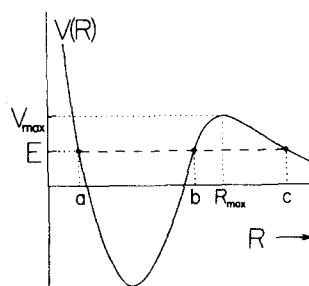


FIG. 1. Schematic potential energy diagram.

<sup>a)</sup>Research supported by the National Research Council of Canada, and in part by a computing grant from the University of Waterloo.

bined with the boundary condition at  $R=0$ , this yields a one-dimensional eigenvalue problem for which the usual predictor-corrector formula<sup>18,19</sup> facilitates rapid convergence to the eigenvalue nearest to the initial trial energy. Of the boundary conditions which have been investigated, the best one<sup>5,17</sup> is the requirement that the wavefunction at the third turning point,  $R=c$ , behaves as an Airy function of the second kind,<sup>20,21</sup>  $\text{Bi}(-z)$ , where  $z = F^{1/3}(R-c)$  and  $F$  is proportional to the slope of the effective potential at  $c$  [see Eq. (3.1)]. Tests showed that for narrow levels, this procedure yields resonance energies in virtually exact agreement with those generated by exact quantum mechanical methods, while for broad levels the discrepancies are usually less than<sup>5,13</sup>  $\sim 0.05\Gamma$  (i. e., "negligible"). However, while well justified empirically, a sound theoretical basis for this boundary condition has not previously appeared. Providing such a foundation is one of the purposes of the present work. To this end, Sec. II of this paper summarizes pertinent parts of the semiclassical theory of orbiting resonances, while Sec. III.A derives the Airy function boundary condition.

A serious limitation of the Airy function boundary condition method is the fact that it works only for levels lying below the potential barrier maximum. While these resonances comprise most of those observed spectroscopically, it would be desirable to have an analogous technique for the very broad resonances lying above  $V_{\text{max}}$ , the ones most readily observed in molecular beam scattering experiments.<sup>22,23</sup> In the latter part of Sec. III, we present and test one such approach, the Weber function boundary condition method.

For the same systems used in testing the Airy and Weber function boundary condition methods, we have also calculated the resonance positions defined by various semiclassical methods, and by the maxima of the collisional time delay function. Comparisons with results obtained using the Weyl-Titchmarsh  $m$ -function technique of Hehenberger *et al.*<sup>11-13</sup> are also reported. The latter appear to show that even for the broadest resonances, the collisional time delay and the  $m$ -function technique predict exactly the same resonance energies.

For very broad resonances, the highly asymmetric behavior of the time delay, internal amplitude and Weyl-Titchmarsh  $m$  function introduces considerable uncertainty regarding the significance of the level widths they define. On the other hand, for extremely narrow resonances, quantum mechanical methods of calculating resonance widths become unreliable because of the loss of numerical precision which tends to accompany the very large change in wave function amplitude across the classically forbidden region,  $b < R < c$ . The fact that these procedures require one to compute the wavefunction into the asymptotic region beyond  $c$  also makes them inconvenient to use in tandem with a boundary condition method for locating quasibound levels. As a result simple semiclassical methods for calculating quasibound level widths have frequently been used. However, while the "primitive" semiclassical method is very accurate for sharp resonances, it is somewhat less reli-

able for broad levels lying near a barrier maximum. Section IV of this paper examines this behavior and presents and tests a number of more sophisticated semiclassical methods for calculating  $\Gamma$ .

## II. THEORY OF ORBITING RESONANCE

The radial wavefunction  $\chi_{EJ}(R)$  for a quasibound state of energy  $E$  and angular momentum quantum number  $J$  satisfies the equation

$$\left[ \frac{d^2}{dR^2} + k^2 - U_J(R) \right] \chi_{EJ}(R) = 0, \quad (2.1)$$

where

$$k^2 = (2\mu/\hbar^2)E, \quad (2.2)$$

$$U_J(R) = (2\mu/\hbar^2)V(R) + J(J+1)/R^2.$$

$V(R)$  is the potential energy function, and the zero of energy is set at the dissociation limit. This wavefunction satisfies the boundary condition  $\chi_{EJ}(0) = 0$  and may be normalized to a delta function in energy so that its asymptotic behavior is given by<sup>2</sup>

$$\chi_{EJ}(R) \underset{R \rightarrow \infty}{\simeq} \chi_{EJ}^{\infty}(R) \equiv (2\mu/\pi\hbar^2k)^{1/2} \sin[kR - J\pi/2 + \eta_J(E)], \quad (2.3)$$

where  $\eta_J(E)$  is the phase shift. The collisional time delay function,  $\tau_d(E, J)$ , is the difference between the time required for an actual collision and the time required for a collision at the same energy if the interaction potential is everywhere zero.<sup>3,4</sup> An exact quantum mechanical expression for it is<sup>3-5</sup>

$$\tau_d(E, J) = 2\hbar \frac{\partial \eta_J}{\partial E} = \int_0^{\infty} (|\chi_{EJ}|^2 - |\chi_{EJ}^{\infty}|^2) dR + (\mu/\hbar k^2) \sin(2\eta_J - J\pi). \quad (2.4)$$

Its rigorous derivation and simple physical interpretation make the behavior of this function particularly attractive for use in defining resonance positions and widths. Therefore, the resonance energies defined by the local maxima of  $\tau_d$  and the widths defined as<sup>5</sup>

$$\Gamma_{td} = 4\hbar/\tau_d^{\text{max}} \quad (2.5)$$

will be used throughout this paper as the "true" values against which other methods will be compared. Improvements to the method of calculating time delays reported in Ref. 5 are described in Appendix A.

The quantity which arises naturally in the semiclassical theory is the internal amplitude function  $A(E, J)$ , describing the wavefunction amplitude in the region between the first two turning points. This is the quantity related to the spectroscopic definition of the resonance position. On the interval  $a \ll R \ll b$ , the JWKB wavefunction may be expressed as<sup>2,5</sup>

$$\chi_{EJ}(R) = A(E, J)\bar{\chi}_{EJ}(R), \quad (2.6)$$

where  $\bar{\chi}_{EJ}(R)$  is a semiclassical bound state wavefunction normalized to unity within the potential well,<sup>2</sup>

$$\bar{\chi}_{EJ}(R) = \left[ \frac{2\mu\hbar\omega}{\pi\hbar^2k_J(R)} \right]^{1/2} \sin\left( \int_a^R k_J(r) dr + \pi/4 \right). \quad (2.7)$$

$[k_J(R)]^2 = k^2 - U_J(R)$ , and  $\hbar\bar{\omega}$  is the local vibrational energy spacing, defined as

$$\hbar\bar{\omega} = (\partial v / \partial E)^{-1}, \quad (2.8)$$

where  $v = v(E, J)$  is defined by the semiclassical quantization condition [Eq. (2.14) below]. The energy dependence of the absorption intensity for a transition of frequency  $\nu$  from a bound state with wavefunction  $\psi_b(R)$  into a quasibound state defined by  $\chi_{EJ}(R)$  is proportional to

$$\nu |\langle \psi_b(R) | M(R) | \chi_{EJ}(R) \rangle|^2,$$

where  $M(R)$  denotes the transition moment function. Use of Eq. (2.6) converts this expression into the form

$$\nu |A(E, J)|^2 |\langle \psi_b | M | \bar{\chi}_{EJ} \rangle|^2,$$

which indicates that the energy dependence of spectroscopic intensities is dominated by that of  $|A(E, J)|^2$ , and hence that spectroscopic resonance energies are determined by its maxima.

The semiclassical wavefunction in the asymptotic region  $R \gg c$  may be written as a linear combination of incoming and outgoing waves:

$$\chi_{EJ}(R) \approx [k_J(R)]^{-1/2} \left\{ C' \exp \left[ i \int_c^R k_J(r) dr \right] + C'' \exp \left[ -i \int_c^R k_J(r) dr \right] \right\}. \quad (2.9)$$

Invoking flux conservation, time reversal symmetry and the asymptotic normalization of Eq. (2.3) yields<sup>2</sup>

$$\left( \frac{C'}{C''} \right) = \frac{1}{2} \left( \frac{2\mu}{\pi \hbar^2 k} \right)^{1/2} \left( \frac{e^{i\delta}}{e^{-i\delta}} \right), \quad (2.10)$$

where

$$\delta = \arctan(e^{-2\tilde{\gamma}} \tan \alpha_J) + (\tilde{\theta} - \tilde{\phi})/2 - \pi/4, \quad (2.11)$$

$$\alpha_J = \int_a^b k_J(r) dr - \frac{1}{2}(\tilde{\phi} + \tilde{\theta}), \quad (2.12)$$

and  $\tilde{\gamma}$ ,  $\tilde{\theta}$ , and  $\tilde{\phi}$  are phase integrals over various parts of the potential. This then allows the internal amplitude function to be expressed as

$$A(E, J) = \{ \hbar\bar{\omega} [\cosh(2\tilde{\gamma}) + \sinh(2\tilde{\gamma}) \cos(2\alpha_J)] \}^{-1/2}. \quad (2.13)$$

Similar semiclassical expressions have also been derived by Miller.<sup>7</sup> It is clear from Eq. (2.13) that if  $\tilde{\gamma}$  is large and neither it nor  $\hbar\bar{\omega}$  vary rapidly with  $E$ ,  $A(E, J)$  will have its maximum when

$$\alpha_J = (v + \frac{1}{2})\pi, \quad (2.14)$$

where  $v$  is the integer denoting the vibrational quantum number. Equation (2.14) is the semiclassical quantization condition for this situation. Substituting this result into Eq. (2.11) then shows that this resonance condition corresponds to

$$\delta_{r_{\text{res}}} = \frac{1}{2}(\tilde{\theta} - \tilde{\phi}) + \frac{1}{4}\pi + n\pi \quad (2.15)$$

for arbitrary integer  $n$ .

### III. METHODS FOR DETERMINING RESONANCE ENERGIES

#### A. The Airy function boundary condition

Consider a case in which the energy  $E$  is sufficiently far below the barrier maximum and above the potential minimum that the turning points  $a$ ,  $b$ , and  $c$  are well separated, and  $U_J(R)$  near  $R = c$  can be approximated by a straight line

$$U_J(R) = k^2 - (R - c)F, \quad (3.1)$$

where  $F = |dU_J/dR|_{R=c}$ . A uniform approximation to  $\chi_{EJ}$  in the region near  $c$  may then be obtained by using the Airy equation as a comparison equation (see Appendix B).<sup>24</sup> The resulting expression for  $\chi_{EJ}(R)$  in the region  $R \gg b$  is

$$\chi_{EJ}(R) = [z(R)/k_J^2(R)]^{1/4} \{ D_1 \text{Ai}(-z) + D_2 \text{Bi}(-z) \}, \quad (3.2)$$

where  $D_1$  and  $D_2$  are independent of  $R$ , and the mapping between  $R$  and  $z$  is given by

$$z^{3/2} = \frac{3}{2} \int_c^R k_J(r) dr. \quad (3.3)$$

Near the turning point  $c$  where (3.1) is valid, Eq. (3.3) reduces to

$$z = (R - c)F^{1/3}. \quad (3.4)$$

For  $R \gg c$ , the asymptotic expressions<sup>20</sup> for Ai and Bi transform Eq. (3.2) into the form:

$$\chi_{EJ}(R) \approx [\pi k_J(R)]^{-1/2} \left\{ D_1 \sin \left[ \int_c^R k_J(r) dr + \frac{\pi}{4} \right] + D_2 \cos \left[ \int_c^R k_J(r) dr + \frac{\pi}{4} \right] \right\}. \quad (3.5)$$

Comparing Eq. (3.5) with Eq. (2.9) and making use of Eq. (2.10) then yields

$$\begin{aligned} D_1 &= (2\mu/\hbar^2 k)^{1/2} \sin(\pi/4 - \delta), \\ D_2 &= (2\mu/\hbar^2 k)^{1/2} \cos(\pi/4 - \delta). \end{aligned} \quad (3.6)$$

Similarly, a linear approximation for  $U_J(R)$  near the second turning point  $b$  also allows  $\chi_{EJ}(R)$  in the region  $a \ll R \ll c$  to be expressed in terms of a linear combination of Airy functions. Connecting (in the region  $b \ll R \ll c$ ) this  $\chi_{EJ}(R)$  with the one given by Eq. (3.2) and constraining it to agree with Eqs. (2.6)–(2.7) in the region  $a \ll R \ll b$  then yields “simple semiclassical” estimates<sup>2,25</sup> for the parameters  $\tilde{\gamma}$ ,  $\tilde{\theta}$ , and  $\tilde{\phi}$ :

$$\tilde{\gamma} = \int_b^c |k_J(r)| dr + \ln(2), \quad (3.7)$$

$$\tilde{\theta} = \tilde{\phi} = 0. \quad (3.8)$$

Substitution of (3.8) into (2.15) then implies that on resonance,  $\delta_{r_{\text{res}}} = \pi/4 + n\pi$ , and hence that  $D_1 = 0$ . Consideration of (3.1) and (3.4) shows that for  $R \approx c$  the factor  $[z(R)/k_J^2(R)]^{1/4}$  appearing in Eq. (3.2) reduces to a constant,  $F^{-1/6}$ . Thus, on resonance the wavefunction near the outermost turning point is simply proportional to the Airy function of the second kind,  $\text{Bi}(-z)$ . This justifies the boundary condition previously proposed by Le Roy and Bernstein.<sup>5</sup> Note that the essential approximation in this derivation is the requirement that the three turning

points  $a$ ,  $b$ , and  $c$  be well separated.

### B. The Weber function boundary condition

If the energy is either above or slightly below the barrier maximum, turning points  $b$  and  $c$  will be either complex or real and very close together, and the above analysis is invalid. For this case, the effective potential in the neighborhood of the barrier maximum may be approximated by a parabola<sup>26</sup>:

$$U_J(R) \approx U_{\max} - \frac{1}{2}\omega_B^2(R - R_{\max})^2, \quad (3.9)$$

where  $R_{\max}$  is the position of the barrier maximum and  $U_{\max} = U_J(R_{\max})$ . The appropriate comparison equation is now the Weber equation<sup>24,25</sup>

$$\left(\frac{d^2}{dz^2} + \epsilon + \frac{z^2}{4}\right)\psi(z) = 0, \quad (3.10)$$

whose solutions are the parabolic cylinder functions.<sup>20</sup> Here,  $\epsilon$  is defined by the requirement that the turning points in  $z$  space and  $R$  space must correspond. For energies below the barrier maximum, it is given by<sup>24,25</sup>

$$\epsilon = (i/\pi) \int_b^c k_J(r) dr = -\frac{1}{\pi} \int_b^c |k_J(r)| dr, \quad (3.11)$$

where the phase of the (imaginary) integrand in Eq. (3.11) is chosen to be  $\pi/2$  so that  $\epsilon$  is real and negative. At these energies the mapping between  $z$  and  $R$  for  $R \gtrsim c$  is given implicitly by

$$\int_c^R k_J(r) dr = \int_{2\sqrt{-\epsilon}}^z (x^2/4 + \epsilon)^{1/2} dx, \quad (3.12)$$

while for  $a \ll R \ll b$  the lower limits of the integrals on the left and right hand sides of Eq. (3.12) become  $b$  and  $-2\sqrt{-\epsilon}$ , respectively. For energies above the barrier maximum, the integration limits in Eq. (3.11) are replaced by the imaginary turning points and  $\epsilon$  becomes positive (and real). At the same time, the lower limits of the integrals on the left and right hand sides of Eq. (3.12) become  $R_{\max}$  and 0, respectively. If Eq. (3.9) is exact, then<sup>26</sup>

$$z = (2\omega_B^2)^{1/4}(R - R_{\max}), \quad (3.13)$$

$$\epsilon = (k^2 - U_{\max})/\sqrt{2}\omega_B = (E - V_{\max})(\sqrt{2}\mu/\hbar^2\omega_B). \quad (3.14)$$

In the present case, the uniform approximation to  $\chi_{EJ}$  (see Appendix B) can be expressed in terms of parabolic cylinder functions<sup>20</sup>:

$$\chi_{EJ}(R) = (dz/dR)^{-1/2} \{P_1 W(-\epsilon, -z) + P_2 W(-\epsilon, z)\}, \quad (3.15)$$

where  $P_1$  and  $P_2$  are independent of  $R$ . Use of the asymptotic expressions<sup>20</sup> for  $W(-\epsilon, \pm z)$  at large  $z$  then transforms Eq. (3.15) into the familiar asymptotic form

$$\chi_{EJ}(R) \approx [\kappa/k_J(R)]^{1/2} \left\{ (P_1/\kappa) \sin \left[ \int_c^R k_J(r) dr - \phi(\epsilon)/2 + \pi/4 \right] + P_2 \cos \left[ \int_c^R k_J(r) dr - \phi(\epsilon)/2 + \pi/4 \right] \right\}, \quad (3.16)$$

where

$$\phi(\epsilon) = \epsilon - \epsilon \ln |\epsilon| + \arg[\Gamma(\frac{1}{2} + i\epsilon)], \quad (3.17)$$

$$\kappa = [1 + e^{-2r\epsilon}]^{1/2} - e^{-r\epsilon} \quad (3.18)$$

Comparing Eq. (3.16) with Eq. (2.9) then shows that

$$P_1 = - (2\mu\kappa/\pi\hbar^2k)^{1/2} \sin(\delta + \phi(\epsilon)/2 - \pi/4) \\ P_2 = (2\mu/\pi\hbar^2k\kappa)^{1/2} \cos(\delta + \phi(\epsilon)/2 - \pi/4). \quad (3.19)$$

When the asymptotic version of Eq. (3.15) for the region  $a \ll R \ll b$  (i.e., the region  $z \ll -2\sqrt{-\epsilon}$ ) is compared with the JWKB expression of Eqs. (2.9)–(2.10), a “uniform quadratic approximation” is obtained for the parameters  $\tilde{\gamma}$ ,  $\tilde{\theta}$ , and  $\tilde{\phi}$ <sup>2,27–29</sup>:

$$\tilde{\gamma} = \cosh^{-1}[1 + e^{-2r\epsilon}]^{1/2}, \quad (3.20)$$

$$\tilde{\phi} = \phi(\epsilon) = \epsilon - \epsilon \ln |\epsilon| + \arg[\Gamma(\frac{1}{2} + i\epsilon)], \quad (3.21)$$

$$\tilde{\theta} = 0. \quad (3.22)$$

On resonance, Eqs. (2.15), (3.21), and (3.22) cause  $P_1$  to vanish, while near the barrier maximum where Eq. (3.13) is accurate, the factor  $(dz/dR)^{-1/2}$  in Eq. (3.15) becomes  $(2\omega_B^2)^{-1/8}$  which is a constant. Thus, on resonance, the wavefunction at  $R \approx R_{\max}$  (i.e., at  $z \approx 0$ ) is simply proportional to a parabolic cylinder function:

$$\chi_{EJ}(R) \propto W(-\epsilon, z). \quad (3.23)$$

This, therefore, is the outer boundary condition for the wave function at a resonance which lies either above or slightly below the potential barrier maximum.

As a consistency check on the above result, it is appropriate to examine its behavior when the turning points are well separated, i.e., at energies far below  $V_{\max}$ . In this limit,  $-\epsilon \gg 0$ , and the appropriate asymptotic expansion for  $W[-\epsilon, z(R)]$  may be used. For the parabolic barrier of Eq. (3.9), it may be shown that near the outermost turning point where  $R = c = 2(2\omega_B^2)^{1/2} \times (-\epsilon)^{1/2}$ ,

$$W[-\epsilon, z(R)] \propto \text{Bi}[-(R - c)F^{1/3}]$$

where  $F = (2\omega_B^2)^{3/4}(-\epsilon)^{1/2}$  is the absolute value of the slope of  $U_J$  at  $c$ . Thus, the Weber function boundary condition does reduce to the Airy function boundary condition for energies well below the maximum of a parabolic barrier.

### C. Other semiclassical methods

The boundary condition methods described above are quantum mechanical in that exact quantal wave functions are computed. However, they are semiclassical in that the choice of the appropriate linear combination of solutions of the comparison equation is based on the semiclassical quantization condition of Eq. (2.14),

$$\left(v + \frac{1}{2}\right)\pi = \int_a^b k_J(r) dr - \frac{1}{2}(\tilde{\phi} + \tilde{\theta}), \quad (3.24)$$

and on the semiclassically derived phase factors of either Eq. (3.8) or Eqs. (3.21)–(3.22). It therefore seems appropriate to compare results obtained using these boundary condition methods to those obtained directly from Eq. (3.24).

Equation (3.24) [or (2.14)] yields a local maximum in the internal amplitude  $A(E, J)$  if  $\tilde{\gamma}$  is large and both it and  $\hbar\tilde{\omega}$  vary slowly with  $E$ . This would not be true for

the broad resonances lying near or above a barrier maximum. Therefore resonance energies obtained using the boundary condition methods and Eq. (3.24) are also compared to those defined by the local maxima of  $A(E, J)$  when the phase factors  $\tilde{\gamma}$ ,  $\tilde{\theta}$ , and  $\tilde{\phi}$  are given by Eqs. (3.20)–(3.22).

#### D. Test of boundary condition and semiclassical methods

In previous work, tests of various methods of calculating resonance positions and widths were based on calculations on particular numerical potential functions for the ground states of  $H_2^5$  or  $HgH^{11-13}$ . To avoid ambiguities due to lack of smoothness or the choice of numerical interpolation procedure, many of the tests reported in the present work utilized a simple analytic potential of the LJ(12, 6) form,

$$V(R) = D_e [(R_e/R)^{12} - 2(R_e/R)^6],$$

where as usual  $D_e$  is the well depth and  $R_e$  the equilibrium distance. The potential parameters were chosen to roughly approximate the isotropic potential for the  $H_2$ -Ar system, for which orbiting resonances have been seen in both spectroscopic<sup>30</sup> and scattering<sup>23</sup> experiments. The equilibrium distance and reduced mass were set at the values  $R_e = 3.56 \text{ \AA}$  and  $\mu = 1.92 \text{ amu}$ , respectively, while the well depth  $D_e$  was varied from 30 to 65  $\text{cm}^{-1}$  in order to shift the calculated resonance energies from below to above the potential barrier maximum.<sup>31</sup>

Use of the Weber function boundary condition requires evaluation of the parameter  $\epsilon$  at each trial energy. For energies  $E < V_{\text{max}}$ , this can be done using Eq. (3.11), while for energies close to and either above or below

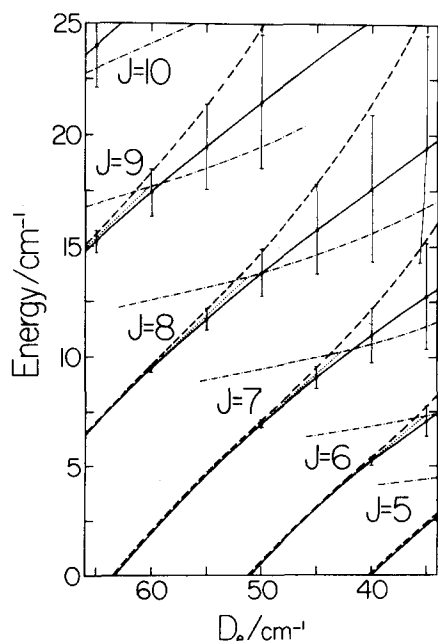


FIG. 2. Resonance energies for various LJ(12, 6) model potentials, as defined by  $\tau_e^{\text{max}}$  (solid curves) and the Airy (dotted curves) and Weber function (dashed curves) boundary conditions. The dot-dash curves correspond to  $V_{\text{max}}$ , while the vertical bars indicate the widths  $\Gamma_{ed}$ .

$V_{\text{max}}$ , a reasonably reliable value of it is given by Eq. (3.14). A somewhat more accurate version of the latter, given by Miller,<sup>32</sup> takes account of barrier asymmetry:

$$\epsilon = (E - V_{\text{max}})(\sqrt{2}\mu/\hbar^2\omega_B)\{1 - (E - V_{\text{max}}) \times [-V_{\text{max}}''' - 5(V_{\text{max}}''')^2/3V_{\text{max}}'']/16(V_{\text{max}}'')^2\} \quad (3.25)$$

In the present work, Eq. (3.11) was used for  $E < V_{\text{max}}$  and Eq. (3.25) for  $E \geq V_{\text{max}}$ . Tests showed that extending use of Eq. (3.25) to energies below  $V_{\text{max}}$  or replacing (3.25) by (3.14) did not significantly affect the results for energies near the barrier maximum.

Use of the semiclassical quantization conditions and internal amplitude maximum criterion requires evaluation of the phase integrals

$$\int_a^b k_r(R)^{\pm 1} dR.$$

Throughout the present work, the turning point  $b$  appearing here was always assumed to be real, and for energies  $E > V_{\text{max}}$  was defined as  $b = R_{\text{max}}$ .

For the LJ(12, 6) model problem, the energies of the  $J = 5-10$  orbiting resonances were calculated for a range of  $D_e$  values. The results are shown in Fig. 2; the dotted and dashed curves were obtained using the Airy and Weber function boundary conditions, respectively, while the solid curves correspond to maxima of  $\tau_e(E, J)$ . The dot-dash curve for each case shows how the corresponding  $V_{\text{max}}$  values depend on  $D_e$ , while the ends of the "error bars" correspond to  $E_r(\tau_e^{\text{max}}) \pm \Gamma_{ed}/2$ .

As expected, the Airy function results are most accurate for energies far below the barrier maximum where the assumption that the turning points are well separated is valid. However, even for levels right at the barrier maximum, their differences with the time delay resonance energies are quite small, approaching a maximum of  $\sim 0.15\Gamma$ . Thus, as found in Refs. 5 and 13, the Airy function boundary condition method appears to be a very reliable way of locating resonances which lie below a barrier maximum. Note, however, that the fact that  $E_r(\text{Airy})$  always lies above  $E_r(\tau_e^{\text{max}})$  is a result specific to this particular type of potential function, as both positive and negative discrepancies for  $E_r(\text{Airy})$  were found in Refs. 5 and 13.

Since the Weber function boundary condition was designed for resonances lying very near  $V_{\text{max}}$ , it is disappointing to see that it performs even worse than the Airy function criterion there. Its derivation is precisely analogous to that for the Airy function criterion, so the fault seems unlikely to lie there. It seems more likely that the difficulty is associated with the semiclassical resonance condition of Eqs. (2.14) and (2.15), whose derivation is based on the assumptions that  $\tilde{\gamma}$  is large and that both  $\tilde{\gamma}$  and  $\hbar\omega$  vary slowly across the width of a resonance. For broad resonances, such assumptions are not valid. In any case, the present results show that the Weber function boundary condition yields resonance energies which are  $\geq \Gamma/2$  too high, and thus it may not be trusted as a method for locating resonances above a barrier maximum.

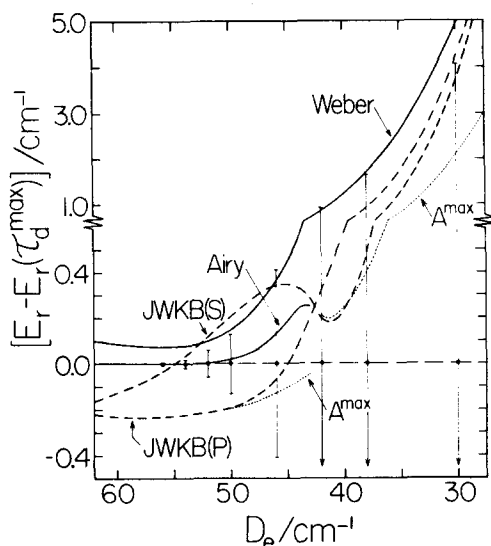


FIG. 3. For the  $J=7$  resonances of Fig. 2, differences from  $E_r(\tau_d^{\max})$  of resonance energies defined by boundary condition methods (solid curves), by the JWKB quantization condition Eq. (3.24) (dashed curves), and by the maxima of the  $A(E, J)$  function of Eq. (2.13) (dashed curve). Note break in vertical scale.

For the  $J=7$  resonance considered above, the difference between the resonance energy  $E_r(\tau_d^{\max})$  determined quantum mechanically and those defined by the boundary condition methods (solid curves), semiclassical internal amplitude (dotted curve), and semiclassical quantization conditions (dashed curves) are shown in more detail in Fig. 3. For resonances lying above  $V_{\max}$ , the energies defined by the maxima of  $A(E, J)$  give the best agreement with the time delay results. It should be noted that  $\tau_d(E, J)$  and  $|A(E, J)|^2$  are expected to have the same functional behavior only if the energy dependence of  $\tilde{\gamma}$  can be neglected.<sup>2</sup> Thus the energies defined by the maxima of  $\tau_d(E, J)$  and  $A(E, J)$  are expected to differ for broad resonances; this occurred in the numerical studies of Ref. 5. Moreover, since the internal amplitude maxima may be related to the spectroscopically observed resonance positions, it is not technically any less "correct" than the position defined by  $\tau_d^{\max}$  (although resonances above a barrier maximum are almost certainly much too broad to be observed spectroscopically). On the other hand, there is no unique quantal definition of the internal amplitude function, and some error in resonance energies predicted using Eq. (2.13) will arise from its semiclassical origin. Moreover, for  $E > V_{\max}$  the approximation that  $b = R_{\max}$  will introduce errors into this result, and is almost certainly responsible for the discontinuity in the  $A(E, J)$  resonance position at the barrier maximum seen in Fig. 3.

The "parabolic" JWKB quantization condition JWKB(P) is obtained by substituting Eqs. (3.21) and (3.22) into Eq. (3.24), while the "simple" JWKB results JWKB(S) correspond to use of Eq. (3.8) in Eq. (3.24). Since Eq. (3.24) is derived from the requirement that  $A(E, J)$  be a maximum by making simplifying assumptions regarding the magnitude and energy dependence of  $\tilde{\gamma}$  and  $\hbar\omega$  (which are certainly valid for  $E \ll V_{\max}$ ), it is not all

surprising to see (in Fig. 3) these three semiclassical methods converge for  $E \ll V_{\max}$ . Their residual difference with the quantal ( $\tau_d^{\max}$ ) results in this region are probably simply due to error inherent in the first order JWKB approximation.

### E. Comparison of time delay and Weyl $m$ -function results

In a recent series of papers, Hehenberger *et al.*<sup>11-13</sup> have derived and applied a scheme for using the poles of the Weyl-Titchmarsh  $m$  function to determine the positions and widths of orbiting resonances. Like the time delay method, the  $m$ -function technique is in principle "exact" in that it involves a unique property of the exact quantum mechanical wave function. On the other hand, there is no simple physical interpretation for the complex  $m$  function or its pole, while use of a complex energy formalism to determine  $\Gamma$  implicitly assumes a Breit-Wigner type of line shape, an approximation which may be quite unrealistic for broad resonances.

As a test of the  $m$ -function method, time delay and Airy function boundary condition calculations have been performed on Stwalley's ICl potential<sup>33</sup> for the ground state of HgH using exactly the same reduced mass and physical constants assumed by Hehenberger *et al.*<sup>11-13,31</sup> For the  $v=1$  orbiting resonances, the energies and widths yielded by the various methods are compared in Table I. These results show that within the numerical accuracy of the  $m$ -function method (as indicated by the differences between the Weyl( $r$ ) and Weyl( $c$ ) energies<sup>12</sup>), the time delay maximum and  $m$ -function methods give exactly the same energies for all resonances, regardless of width. Similar agreement was found for all of the other HgH resonance energies reported by Hehenberger *et al.*<sup>11-13</sup> The complexities of the Weyl-Titchmarsh theory make the formal equivalence of these methods difficult to prove, but the excellent agreement of the energies for resonances with widths ranging over several orders of magnitude suggest that the two methods are very closely related. The quality of agreement with the Airy boundary condition method is similar to that found above and in Ref. 13.

For narrow resonances, the widths obtained from the time delay maximum and  $m$ -function methods show the same exact agreement found for the resonance positions, but small discrepancies grow in with increasing resonance width. These differences probably reflect the incipient breakdown of the Breit-Wigner parameterization implicit in the complex energy formalism used in the  $m$ -function method. However, even for the broadest levels the differences are sufficiently small fractions of the width that they may be deemed "insignificant."

In conclusion, therefore, it appears that the time delay maximum and  $m$ -function methods yield essentially the same resonance position and widths for all cases. Both are less efficient than boundary condition methods in that they require the wavefunction to be numerically integrated into the asymptotic region where the noncentrifugal part of the potential is negligible, and they include no second-order type process for automatically

TABLE I. Comparison of Weyl  $m$ -function and time delay maximum methods for the  $\nu = 1$  resonances of ground state Hg-H.

$\nu$	$J$	$V_{\max}/\text{cm}^{-1}$	$\tau_d^{\max}$	$E_r/\text{cm}^{-1}$				$\Gamma/\text{cm}^{-1}$		
				Weyl( $r$ ) <sup>a</sup>	Weyl( $c$ ) <sup>a</sup>	Airy B.C.	$\Gamma_{td}$	Weyl( $r$ ) <sup>a</sup>	Weyl( $c$ ) <sup>a</sup>	$\Gamma_{MC}$ <sup>d</sup>
1	20	729.67	b	161.47	...	161.47	b	9.85(-11)	...	10.46(-11)
1	21	827.54	b	347.41	...	347.41	b	1.89(-5)	...	1.91(-5)
1	22	931.90	539.13	539.13	...	539.13	5.42(-3)	5.42(-3)	...	5.02(-3)
1	23	1042.82	735.68	735.68	...	735.69	0.129	0.129	...	0.127
1	24	1160.42	935.67	935.67	...	935.69	1.23 <sub>5</sub>	1.23 <sub>5</sub>	...	1.15
1	25	1284.83	1137.55	1137.55	...	1137.52	6.12	6.14	...	5.95
1	26	1416.64	1340.44	1340.43	...	1341.12	19.6	19.8	...	20.1
1	27	1565.32	1545.25	1545.07	1545.23	1546.66	46.9	48.3	48.3	57.1
1	28	1724.97	1754.40	1753.43	1754.67	c	89.4	95.3	93.8	95.7
1	29	1891.64	1969.01	1964.45	1969.55	c	147	171	154	105

<sup>a</sup>From Refs. 11 and 12; Weyl( $c$ ) results were not reported for  $J = 20-26$ , but are presumably identical to the Weyl( $r$ ) results there.

<sup>b</sup>This method is difficult to use for very narrow resonances.

<sup>c</sup>This method does not work for levels above a barrier maximum.

<sup>d</sup> $\Gamma_{MC}$  values calculated at the Weyl( $r$ ) energies; see Sec. IV.<sup>36</sup>

converging on a resonance. However, while computing the time delay requires calculation of only the regular solution of the radial Schrödinger equation, the [Weyl( $c$ )] version of the  $m$ -function method required for broad resonances<sup>12</sup> requires both linearly independent solutions and their derivatives. Together with the existence of a simple physical interpretation for it, the concomitant saving in computer time makes the time delay maximum method the better way of calculating the positions and widths of broad resonances. As with the Weyl( $c$ ) method, the time delay method has no difficulty in separately resolving broad overlapping resonances such as the  $J = 9$ ,  $\nu = 3$ , and 4 levels of HgH.

#### IV. CALCULATION OF RESONANCE WIDTHS (PREDISSOCIATION LIFETIMES)

##### A. General

The width ( $\Gamma$ ) or predissociation lifetime ( $\tau = \hbar/\Gamma$ ) of a quasibound level is a somewhat ambiguous quantity, in that its measured value will in general depend partially on how the state was prepared and how it is observed. For narrow (sharp) resonances where a Breit-Wigner parameterization is possible, it has been shown analytically and verified numerically that various definitions of the width yield essentially the same results.<sup>2,5</sup> On the other hand, the work of Ref. 5 showed that "quantal" values of the level width defined as the full width at half maximum of the internal amplitude function or time delay function, and the quantity  $\Gamma_{td}$  defined by Eq. (2.5) could differ significantly for broad resonances.<sup>5</sup> Hehenberger *et al.*<sup>12</sup> have also shown that different versions of their  $m$ -function method give slightly different results for very broad resonances, and the comparisons in Table I show that these may also differ from  $\Gamma_{td}$  values calculated from Eq. (2.5). However, in the present work its ease of computation<sup>34</sup> and simple physical interpretation have led us to treat  $\Gamma_{td}$  as the "true" width of a given resonance.

##### B. Semiclassical theory of resonance widths

Although  $\Gamma_{td}$  is probably the best objective measure of a resonance width, for the reasons given in Sec. I it

would often be more convenient to use a semiclassical method of estimating this quantity. The most primitive approach would be to define the width as the ratio of the probability per collision of transmission through the potential barrier to the period of oscillation in the potential well<sup>2,5</sup>:

$$\Gamma_0 = \hbar e^{2\pi\epsilon} / t_{v1b} = (\hbar\omega/2\pi) e^{2\pi\epsilon}, \quad (4.1)$$

where  $\hbar\omega$  is given by

$$\hbar\omega = (\pi\hbar^2/\mu) \left\{ \int_a^b [k_J(r)]^{-1} dr \right\}^{-1}, \quad (4.2)$$

and  $\epsilon$  by either (3.11) for  $E < V_{\max}$  or (3.25) for  $E \geq V_{\max}$ . Equation (4.2) is obtained from Eqs. (2.8), (2.12), and (2.14) by using the "simple" semiclassical results of (3.8). An improved version of this result has also been proposed<sup>2,28</sup>:

$$\Gamma_1 = (\hbar\omega/2\pi) \ln(1 + e^{2\pi\epsilon}). \quad (4.3)$$

While both (4.1) and (4.3) yield reasonable widths for levels not too near a potential maximum,<sup>2,5,9,13</sup> consideration of Eq. (4.2) shows that if  $E = V_{\max}$ ,  $\hbar\omega$  vanishes, making both  $\Gamma_0$  and  $\Gamma_1$  equal to zero. However, Child has pointed out<sup>35</sup> that the factor  $\hbar\omega$  appearing in these expressions should be evaluated consistently within the uniform parabolic approximation. Thus, from Eq. (2.8) and the quantization condition (2.14), one obtains

$$\hbar\omega = \pi(\partial\alpha_J/\partial E)^{-1}, \quad (4.4)$$

where  $\alpha_J$  given by Eq. (2.12) is calculated using Eqs. (3.21)–(3.22). The energy dependence of  $\phi(\epsilon)$  cancels out the singularity in the integral in Eq. (4.2) so that the resulting level width

$$\Gamma_{MC} = (\hbar\omega/2\pi) \ln(1 + e^{2\pi\epsilon}) \quad (4.5)$$

remains finite and nonzero for resonances near or at a potential barrier maximum.

A more general approach to the problem of the artificial zeros in  $\Gamma_0$  and  $\Gamma_1$  could be based on the complex energy formalism of Connor.<sup>28,29</sup> In this approach, the eigenvalue criterion for a resonance energy is given by [Eq. (13) of Ref. 29]

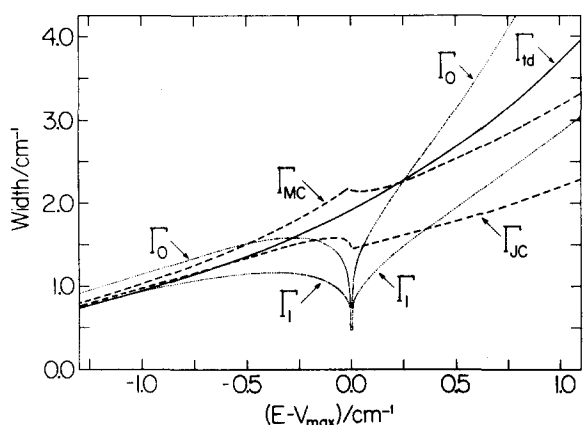


FIG. 4. Comparison of semiclassically calculated resonance widths with  $\Gamma_{td}$  for the  $J=7$  LJ(12,6) resonances of Figs. 2 and 3.

$$\int_a^b k_J(R) dR = (v + \frac{1}{2})\pi + \frac{1}{2}\phi(\epsilon) - \frac{i}{4} \ln(1 + e^{2\pi\epsilon}) - \frac{i}{2} \ln[f(\epsilon)], \quad (4.6)$$

where  $v$  is a non-negative integer and

$$f(\epsilon) = |\Gamma(\frac{1}{2} + i\epsilon)| [\cosh(\pi\epsilon)/\pi]^{1/2} \quad (4.7)$$

When  $\epsilon$  is real,  $f(\epsilon)$  becomes unity. Defining the complex energy as

$$E = E_r - i\Gamma/2 \quad (4.8)$$

the parabolic approximation allows  $\epsilon$  to be written as

$$\epsilon = \epsilon_r + i\epsilon_i = (E_r - V_{\max})/\hbar\omega_B^* - i(\Gamma/2)/\hbar\omega_B^*, \quad (4.9)$$

where  $\omega_B^* = \hbar\omega_B/\sqrt{2}\mu$ .<sup>26</sup> Strictly speaking, the turning points  $a$  and  $b$  appearing in the left-hand side of Eq. (4.6) are complex numbers, since they are the roots of the equation

$$E_r - i\Gamma/2 = V_J(R), \quad (4.10)$$

where  $V_J(R) = (\hbar^2/2\mu)U_J(R)$ . To avoid doing calculation in the complex plane, we make the assumption that  $a$  and  $b$  can be replaced by the corresponding real turning points when the system has (the real) energy  $E_r$ , and that  $b = R_{\max}$  for  $E_r > V_{\max}$ .

If (4.6) is decomposed into its real and imaginary parts, the latter is then (exactly) given by

$$\begin{aligned} (\mu/\hbar^2)^{1/2} \int_a^b \{ [E_r - V_J(R)]^2 + (\Gamma/2)^2 \}^{1/2} - [E_r - V_J(R)]^{1/2} dR \\ = \frac{1}{8} \ln[1 + 2e^{2\pi\epsilon_r} \cos(2\pi\epsilon_i) + e^{4\pi\epsilon_r}] \\ - \frac{1}{2} \text{Im}[\phi(\epsilon)] + \frac{1}{2} R I[\ln f(\epsilon)], \end{aligned} \quad (4.11)$$

where

$$\text{Im}[\phi(\epsilon)] = \epsilon_i [1 - \frac{1}{2} \ln(\epsilon_r^2 + \epsilon_i^2)] - \epsilon_r \arctan(\epsilon_i/\epsilon_r), \quad (4.12)$$

$$\begin{aligned} R I[\ln f(\epsilon)] = \frac{1}{2} \ln |\Gamma(\frac{1}{2} - \epsilon_i + i\epsilon_r)|^2 - \frac{1}{2} \ln(\pi) \\ + \frac{1}{4} \ln[\sinh^2(\pi\epsilon_r) + \cos^2(\pi\epsilon_i)]. \end{aligned} \quad (4.13)$$

Use of (4.9) allows all of the quantities appearing in (4.11) to be readily evaluated for any given values of  $E_r$  and  $\Gamma$ . Thus, at any chosen estimate of the resonance

energy  $E_r$ , Eq. (4.11) may be (iteratively) solved to yield a corresponding value of  $\Gamma$ . The resonance width thus obtained from the eigenvalue criterion of Eq. (4.6) is denoted by  $\Gamma_{JC}$ . Note that use of the two approximations: (i)  $\epsilon_i = 0$ , and (ii)  $\Gamma \ll [E - V_J(R)]$  wherever the integrand makes a significant contribution to the integral in Eq. (4.11), collapses  $\Gamma_{JC}$  to  $\Gamma_1$ , while for  $e^{2\pi\epsilon} \ll 1$ ,  $\Gamma_1$  collapses to  $\Gamma_0$ .

### C. Tests of the semiclassical resonance widths

For the same LJ(12,6) model problem described in Sec. III.D, values of the four semiclassical resonance widths  $\Gamma_0$ ,  $\Gamma_1$ ,  $\Gamma_{MC}$ , and  $\Gamma_{JC}$  were calculated at the energies  $E_r(\tau_d^{\max})$ . In Fig. 4, these results for  $J=7$  are compared with each other and with  $\Gamma_{td}$ . As expected,  $\Gamma_0$  and  $\Gamma_1$  go to zero as  $E$  approaches  $V_{\max}$ . While  $\Gamma_{JC}$  and  $\Gamma_{MC}$  avoid this artificial zero, their values show discontinuous first derivatives at  $E = V_{\max}$ . This probably reflects the error associated with the use of a real outer turning point  $b = R_{\max}$  in the integrals of Eqs. (4.2) and (4.11), for  $E > V_{\max}$ . This approximation is probably also responsible for their increasing deviation from the  $\Gamma_{td}$  values for energies above  $V_{\max}$ . In any case, it seems clear that the best overall results are those obtained from the expression Eq. (4.5) suggested by Child.<sup>35</sup>

In previous work,<sup>2</sup> Child compared  $\Gamma_0$  and  $\Gamma_1$  values with the full width at half maxima of the internal amplitude function for ground state  $H_2$ . For exactly the same states, the present Table II compares our four semiclassical methods with  $\Gamma_{td}$  (again, these widths were calculated at the resonance energy defined by  $\tau_d^{\max}$ ). Once again, the average of the errors in the  $\Gamma_{MC}$  values (of 0.026 $\Gamma$ ) is significantly smaller than those for the other semiclassical methods. For the sake of completeness, Table I also includes values of  $\Gamma_{MC}$  for the  $v=1$  resonances of HgH.<sup>36</sup> In keeping with the results of Fig. 4 and Table II,  $\Gamma_{MC}$  is quite accurate for sharp resonances but increasingly unreliable for those lying above the barrier maximum.

### V. CONCLUDING REMARKS

The present study has shown that the two quantum mechanical methods of calculating resonance positions and widths, the time delay maximum and  $m$ -function

TABLE II. Comparison of calculated resonance widths for various levels of ground state  $H_2$ ; <sup>a</sup> energies in  $\text{cm}^{-1}$ .

$v$	$J$	$\hbar\bar{\omega}$	$\Gamma_0$	$\Gamma_1$	$\Gamma_{JC}$	$\Gamma_{MC}$	$\Gamma_{td}$
0	38	871	87.0	64.4	85.2	79.9	80.0
1	35	1003	14.9	14.2	13.9	13.6	14.1
2	33	937	22.4	21.0	20.5	20.1	20.4
3	31	885	26.6	24.5	24.0	23.6	23.6
4	29	835	28.2	25.7	25.4	24.8	24.7
5	27	783	29.1	26.2	26.1	25.5	25.1
6	25	724	31.1	27.6	27.6	27.0	26.5
7	23	659	36.3	31.1	31.7	31.4	30.4
8	21	589	46.9	37.3	41.8	41.1	39.4
11	14	416	21.4	18.6	18.3	18.5	17.9

<sup>a</sup>Calculations performed using exactly the same potential and physical constants as Ref. 5.



techniques, are practically equivalent. However, neither of these methods is numerically stable for extremely narrow resonances (although the  $m$ -function certainly appears to be more tolerant in this regard). On the other hand, the Airy function boundary condition method combined with a semiclassical calculation of the width  $\Gamma_{MC}$  is readily applicable and highly accurate for the sharpest of resonances, and is only slightly less than ideal for the worst case to which it can be applied (levels only slightly below a barrier maximum). Therefore, in view of its simple physical interpretation and lesser computational expense, we conclude that the time delay maximum method is the best method for treating resonances above (or near) a barrier maximum, while the Airy function boundary condition plus  $\Gamma_{MC}$  width calculation is preferable for sharp resonances at energies below  $V_{\max}$ .<sup>34</sup>

### ACKNOWLEDGMENT

We are very grateful to M. S. Child for suggesting the use of  $\hbar\omega$  in calculations of semiclassical level widths. We are also indebted to W. C. Stwalley for sending us the program for generating his HgH potential, and to M. Hehenberger and J. N. L. Connor for helpful correspondence. One of the authors (W. K. L.) is grateful to F. R. McCourt for his encouragement and financial support during the course of this work.

### APPENDIX A. IMPROVEMENTS TO THE METHOD FOR CALCULATING $\tau_d(E, J)$

This appendix describes improvements to the method for calculating the collisional time delay which was presented in Appendix A of Ref. 5; familiarity with the notations and results of Ref. 5 is assumed.

While the procedure for evaluating  $\Delta(Z_*, J)$  from Eq. (A8) is basically sound, numerical problems of computer overflows and underflows may hamper its application to cases where  $J$  is large. These problems arise because for large  $J$  and  $m$ , the Rayleigh expansion coefficients  $N_J^m$  and the quantities  $A_J^m$ ,  $B_J^m$ , and  $C_J^m$  derived from them become very large, while the integrals with which these factors are multiplied,  $S(2m-1)$  and  $C(2m)$ , become very small. Introduction of the normalized expansion coefficient  $\bar{N}_J^m \equiv N_J^m/J^m$  effectively removes this problem. The ensuing revised versions of Eqs. (A7) and (A8) from Ref. 5 are:

$$\bar{N}_J^m = [\bar{N}_{J-1}^m - \bar{N}_{J-1}^{m-1}(J-1+m)/(J-1)](1-1/J)^m, \quad (\text{A7}')$$

and

$$\Delta(Z_*, J) = \left(\frac{4\mu}{\hbar k}\right) \sum_{m=1}^J \{ \bar{A}_J^m \bar{S}(2m-1) + \bar{B}_J^m \bar{C}(2m) + \bar{C}_J^m Z_*(J/Z_*)^{2m} \}, \quad (\text{A8}')$$

where

$$\begin{aligned} \bar{A}_J^m &= A_J^m/(J)^{2m} = [(-1)^{J-m}/J] \\ &\times \sum_{n=1}^{\min(m, J-m+1)} \bar{N}_J^{m+n-1} \bar{N}_J^{m-n}, \\ \bar{B}_J^m &= B_J^m/(J)^{2m} = (-1)^{J-m} \left\{ \frac{1}{2} (\bar{N}_J^m)^2 + \sum_{n=1}^{\min(m, J-m)} \bar{N}_J^{m+n} \bar{N}_J^{m-n} \right\}, \end{aligned}$$

$$\begin{aligned} \bar{C}_J^m &= C_J^m/(J)^{2m} = (2m-1)^{-1} \left\{ \frac{1}{2} (\bar{N}_J^m)^2 \right. \\ &\left. + \sum_{n=1}^{\min(m, J-m)} (-1)^n \bar{N}_J^{m+n} \bar{N}_J^{m-n} \right\} \end{aligned} \quad (\text{A9}')$$

while  $\bar{C}(2m) \equiv (J)^{2m} C(2m)$  and  $\bar{S}(2m-1) \equiv (J)^{2m} S(2m-1)$ . This renormalization changes the recursion relations of Eqs. (A10) to

$$\begin{aligned} \bar{C}(2m) &= -\frac{1}{2} \sin(2Z_* + 2\eta_J)(J/Z_*)^{2m} + m \bar{S}(2m+1)/J^2, \\ \bar{S}(2m-1) &= \frac{1}{2} J \cos(2Z_* + 2\eta_J)(J/Z_*)^{2m-1} - (m - \frac{1}{2}) \bar{C}(2m). \end{aligned} \quad (\text{A10}')$$

A second point concerns the determination of a reliable value of  $\bar{C}(2J)$  or  $\bar{S}(1)$  to initiate use of the recursion relations of Eqs. (A10)'. This turns out to be a nonproblem. Numerical tests show that (to machine accuracy, for us 15 digits) values of  $\Delta(Z_*, J)$  obtained from Eq. (A8)' are independent of the values of  $\bar{C}(2m)$  and  $\bar{S}(2m-1)$  as long as the latter are all interrelated by the recursion relations of Eqs. (A10)'. Attempts to prove this formally have been unsuccessful, but tests for a wide range of cases have convinced us that this is true. In order to minimize loss of precision due to products such as  $\bar{B}_J^m \times \bar{C}(2m)$  becoming much larger than the sum in Eq. (A8)', it was found to be best to initiate the recursion relation at  $m=J$  with a very small value for  $\bar{C}(2J)$ , such as  $\bar{C}(2J) = 0$ .

### APPENDIX B. UNIFORM APPROXIMATION

The uniform approximation is basically a generalization of the JWKB method for the solution of a differential equation

$$\left[ \frac{d^2}{dR^2} + \Lambda(R) \right] \psi(R) = 0. \quad (\text{B1})$$

The results of Sec. 4.1 of Ref. 24 will be summarized here. If there exists a second differential equation

$$\left[ \frac{d^2}{dz^2} + \Omega(z) \right] \phi(z) = 0 \quad (\text{B2})$$

whose solutions are known, where  $\Omega(z)$  is similar to  $\Lambda(R)$ , then a mapping between  $R$  and  $z$  can be defined implicitly by

$$\int_{z_0}^z \Omega(z')^{1/2} dz' = \int_{R_0}^R \Lambda(R')^{1/2} dR', \quad (\text{B3})$$

where  $R_0$  and  $z_0$  are "equivalent," and are usually chosen to be the corresponding points where  $\Lambda(R)$  and  $\Omega(z)$  vanish. Equation (B2) is called the *comparison equation*, and an approximation to  $\psi$  can be given in terms of  $\phi$  by

$$\psi(R) = \{ \Omega[z(R)] / \Lambda(R) \}^{1/4} \phi[z(R)]. \quad (\text{B4})$$

For further detail, see Ref. 24.

<sup>1</sup>See, e.g., Figs 2 and 3 in the paper by R. A. Buckingham and J. W. Fox [Proc. R. Soc. A287, 102 (1962)], noting that normalized continuum wave functions at neighboring energies have virtually the same asymptotic amplitude.

<sup>2</sup>M. S. Child, *Molecular Spectroscopy II* [a Specialist Periodical Report of the Chemical Society (London)], edited by R. F. Barrow, D. A. Long, and D. J. Millen (Chemical Society, London, 1974), pp. 466-512.

<sup>3</sup>E. P. Wigner, Phys. Rev. 98, 145 (1955).

- <sup>4</sup>F. T. Smith, Phys. Rev. **118**, 349 (1960); Erratum **119**, 2098 (1960).
- <sup>5</sup>R. J. Le Roy and R. B. Bernstein, J. Chem. Phys. **54**, 5114 (1971). Corrigenda: (i) in Eq. (15) the factor  $(2/\mu)^{1/2}$  should have read  $(2\mu)^{1/2}$ , and (ii) the labels on columns 5 and 6 of Table III should be "Airy( $R_3$ )" and "WKB( $R_{\max}$ )," respectively.
- <sup>6</sup>A. C. Allison, Chem. Phys. Lett. **3**, 371 (1969).
- <sup>7</sup>W. H. Miller, J. Chem. Phys. **50**, 931 (1969).
- <sup>8</sup>J. L. Jackson and R. E. Wyatt, Chem. Phys. Lett. **4**, 643 (1970).
- <sup>9</sup>R. A. Bain and J. N. Bardsley, J. Chem. Phys. **55**, 4535 (1971).
- <sup>10</sup>A. J. F. Siegert, Phys. Rev. **56**, 750 (1939).
- <sup>11</sup>M. Hehenberger, B. Laskowski, and E. Brändas, J. Chem. Phys. **65**, 4559 (1976).
- <sup>12</sup>M. Hehenberger, P. Froelich and E. Brändas, J. Chem. Phys. **65**, 4571 (1976).
- <sup>13</sup>M. Hehenberger, J. Chem. Phys. **67**, 1710 (1977).
- <sup>14</sup>Defined roughly as those having a predissociation lifetime of  $\tau \lesssim 10^{-11}$  sec (a width of  $\Gamma \gtrsim 0.5$  cm<sup>-1</sup>.)
- <sup>15</sup>R. B. Bernstein, C. F. Curtiss, S. Imam-Rahajoe, and H. T. Wood, J. Chem. Phys. **44**, 4072 (1966).
- <sup>16</sup>B. C. Eu and J. Ross, J. Chem. Phys. **44**, 2467 (1966).
- <sup>17</sup>W. Kołos and J. M. Peek, Chem. Phys. **12**, 381 (1976).
- <sup>18</sup>J. W. Cooley, Math. Comput. **15**, 363 (1961).
- <sup>19</sup>J. K. Cashion, J. Chem. Phys. **39**, 1872 (1963).
- <sup>20</sup>A. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1968).
- <sup>21</sup>Equation 10.4.3 of Ref. 20 provides a simple power series expression for Bi( $x$ ) which should be highly accurate for  $R \approx R_3(E)$ .
- <sup>22</sup>(a) A. Schutte, D. Bassi, F. Tommasini, and G. Scoles, Phys. Rev. Lett. **29**, 979 (1972); (b) J. Chem. Phys. **62**, 600 (1975).
- <sup>23</sup>(a) J. P. Toemies, W. Welz, and G. Wolf, J. Chem. Phys. **64**, 5305 (1976); (b) G. Wolf, Dissertation, Max-Planck-Institut für Stromungsforschung, 1976 (unpublished).
- <sup>24</sup>M. V. Berry and K. E. Mount, Rep. Prog. Phys. **35**, 315 (1972), and references therein.
- <sup>25</sup>M. V. Berry, Proc. Phys. Soc. (London) **88**, 285 (1966).
- <sup>26</sup>Note that our notation differs slightly from that of Child<sup>2</sup> in that his  $\hbar\omega_J^*$  is replaced by our  $\hbar\omega_B = \hbar^2\omega_B/2^{1/2}\mu$ . Similarly, his  $\Gamma^{(0)}$  and  $\Gamma^{(1)}$  are herein replaced by  $\Gamma_0$  and  $\Gamma_1$ , respectively.
- <sup>27</sup>J. N. L. Connor, Mol. Phys. **15**, 37 (1968).
- <sup>28</sup>J. N. L. Connor, Mol. Phys. **15**, 621 (1968).
- <sup>29</sup>J. N. L. Connor, Mol. Phys. **25**, 1469 (1973).
- <sup>30</sup>A. R. W. McKellar and H. L. Welsh, J. Chem. Phys. **55**, 595 (1971).
- <sup>31</sup>In all calculations except those for HgH, the fundamental physical constants were represented by the factor  $\hbar^2/2m = 16.857630$  amu cm<sup>-1</sup> Å<sup>2</sup> where  $m$  is a mass of 1 amu. For consistency with the HgH calculation of Hehenberger *et al.*,<sup>11-13</sup> the value 16.8580077 amu cm<sup>-1</sup> Å<sup>2</sup> is used for this factor in the HgH calculation, with  $\mu(\text{HgH}) = 1.002462$  amu.
- <sup>32</sup>W. H. Miller, J. Chem. Phys. **48**, 1651 (1968).
- <sup>33</sup>W. C. Stwalley, J. Chem. Phys. **63**, 3062 (1975).
- <sup>34</sup>Listings of programs for calculating  $\tau_d(E, J)$  and for determining the positions and widths of resonances using the time delay maximum or Airy function plus  $\Gamma_{MC}$  methods are available on request as University of Waterloo Chemical Physics Research Reports CP-107 and CP-110 (1978), respectively.
- <sup>35</sup>M. S. Child (private communication, 1977).
- <sup>36</sup>While the  $\Gamma_{MC}$  values in Table I were calculated at the Weyl( $\tau$ ) energies, the analogous values at the Airy boundary condition eigenvalues are all identical except that for  $J=26$  and  $27$ ,  $\Gamma_{MC}$  (Airy) = 20.3 and 58.8 cm<sup>-1</sup>, respectively.