Double Wells*

Evans M. Harrell

Department of Mathematics, The Johns Hopkins University, Baltimore, MD 21218, USA

Abstract. Schrödinger operators with interactions symmetric about a plane (double-well potentials) occur in several branches of physics, such as chemistry and quantum field theory. They commonly exhibit asymptotic eigenvalue degeneracy, i.e., pairs of eigenvalues coalesce as the potential wells get farther apart. After a sketch of the theory of double wells, it is shown that the problem of estimating the gap between two such eigenvalues is reducible to finding asymptotics of eigenfunctions. For several examples and classes of potentials the gap is estimated or bounded above and below. The general case is fully n-dimensional.

I. Introduction

It is well known that if a potential $V(\mathbf{x})$ with two minima is symmetric under reflection through a plane (hyperplane, if $N > 3$), then the eigenvalues of the Schrödinger operator

$$-\Delta + V \quad \text{on} \quad L^2(\mathbb{R}^N) \tag{1.1}$$

tend to group in pairs (possibly after restriction to some symmetry subspace). In the simplest case, V has two equivalent, widely separated minima. The physical explanation for the grouping is that the particle evolving according to the Hamiltonian (1.1) could be localized near either well (minimum) in approximately the state it might be in if the second well did not exist. To some degree of accuracy there will be a two-fold degeneracy because of the possibility of being at either well. However, the presence of the second well has two weak effects, a) that the actual eigenstates must be even or odd about the central plane, in chemical language, they must be gerade (g) or ungerade (u); and b) that the degeneracy is split by the perturbation, making the antisymmetric state lie slightly above the

symmetric one. The magnitude of the splitting is typically exponentially small in the relevant parameter, the separation R between the wells; semiclassical arguments indicate that in the simplest cases the gap is on the order of

$$R^a \exp(-kR^b) \tag{1.2}$$

for some a, $b > 0$, and $k > 0$. For this reason it is hopeless to try to compute the splitting by any perturbative series expansion in $1/R$. After discussing the general properties and history of double wells, this article will derive rigorous formulae for the splittings in a fairly general setting and any finite dimensionality, and will then evaluate those formulae in several representative cases. Two examples, the anharmonic oscillator and the hydrogen molecular ion H_2^+, are discussed in detail in Sects. III and IV.

Double-well potentials are practically ubiquitous in physics, but are particularly of interest in three branches, quantum field theory, statistical mechanics, and molecular chemistry.

Quantum Field Theory

Schrödinger operators with double-well potentials are thought to be a fruitful model for understanding gauge fields with degenerate vacua. The vacua would be independent but for weak, semiclassical tunnelings between them, known as instantons. The stability of the false vacuum, unfavored by the coupling, is inversely related to the eigenvalue gap. This is entertainingly discussed by Coleman [19], who compares instanton and WKB analyses of the splitting for one-dimensional anharmonic oscillators, and gives references to the literature. The WKB analysis of the gap for the one-dimensional anharmonic oscillator was made rigorous in [2]. The limit as the dimension $n \to \infty$ would be interesting. See also related work in [3–5].

Statistical Mechanics

It has been argued by Kac [6] that there is a very general relationship between the existence of long-range order in statistical mechanical systems and the degeneracy or near degeneracy of the eigenvalues of certain operators related to the transfer matrix. Kac's argument elaborates on ideas of Ashkin and Lamb [7] and Newell and Montroll [8], and as an example he showed that under fairly wild approximations the existence of long-range order of a certain spin system was equivalent to the asymptotic eigenvalue degeneracy of the same one-dimensional anharmonic oscillator studied by the quantum field theorists mentioned above. In addition, the problem has been studied in [9] from the statistical-mechanical point of view. The rate of asymptotic eigenvalue degeneracy would be related to critical behavior at a phase transition.

Molecular Chemistry

It is in this field that the subject of double-well potentials has the longest history. They model diatomic, homopolar molecules such as H_2^+ or O_2, at least in the approximation of infinite nuclear masses (i.e., stationary centers of force) and, in

more complicated molecules than H_2^+, averaged interelectronic forces. These two approximations are standard, so not much comment will be made on them. The latter is, of course, most trustworthy in the case of a diatomic ion with filled shells and one valence electron. Spin interaction, relativistic corrections, and the like are extraneous to the central mathematical problem of this article, and will be ignored (see [10, 11]). One of the key formulae, (2.3), applies to any quantum particle in a potential having bilateral symmetry, and thus to a wider set of chemical problems, such as the decay of right-handed to left-handed molecules, but only the case of diatomic molecules will be dealt with below. The splitting in the energy levels of the g and u states is a quantum phenomenon, and has no analogy in the related classical problem of a planet orbiting two suns [12, 13], nor even in the old quantum theory (H_2^+ was the subject of Pauli's doctoral dissertation [14]). However, once it was recognized that in wave mechanics a particle could tunnel from one well to another, the classical and old quantum analyses were useful for showing that the simplest case, H_2^+, was separable in elliptic coordinates, and it soon became the most popular diatomic molecule for theoretical study. The first correct analysis of the separated equations was by Jaffé [15], who, however, did not attempt to compute the eigenvalue gap. Hydrogen molecular wave functions have been tabulated in [16], and the first accurate computation of the gap is due to Herring [11], who reports that LCAO calculations are off by about 10% at large internuclear distances (see also [17, 18]). The hydrogen molecular ion will be analyzed as an example below.

The general definitions and convergence theorems have been discussed by Aventini and Seiler [19], Combes and Seiler [20], and Morgan and Simon [21].

To fix notation, the relevant facts are collected here.

Definition (1.3). Two unitary operations that will be used frequently are:

$$[T_a g](x_1, x_2, \ldots) \equiv g(x_1 + a, x_2, \ldots) \tag{1.4}$$

and

$$[\mathscr{R} g](x_1, x_2, \ldots) \equiv g(-x_1, x_2, \ldots). \tag{1.5}$$

Definition (1.6). The class $\mathscr{V}$ of potentials most frequently considered below consists of real-valued $V(x) \in L^r + (L^\infty)_\varepsilon$ on $\mathbb{R}^n$ (i.e., for all $\varepsilon > 0$, $V = A + B$, where $\|A\|_r < \infty$, $\|B\|_\infty < \varepsilon$), for all r such that $1 \leq r \leq q$, q some number $\geq \max(n/2, 2)$ for $n \neq 4$, $q > 2$ if $n = 4$.

Also let $\mathscr{V}_s$ be the potentials of V that are C^∞ for all $\mathbf{x} : |\mathbf{x}| > b$, some finite number, and which $\to 0$ as $|\mathbf{x}| \to \infty$.

Remarks. 1. These potentials are slightly more restrictive than being relatively compact, which needs only $r = q$. Having all $r \in [1, q]$ is essentially a locality assumption, and can probably be relaxed. $\mathscr{V}_s$ includes Coulomb and most other potentials of interest in the molecular case for one electron ($V \to 0$ at ∞).

2. The double-well potential is typically a sum of single-well potentials,

$$W_f = V_r + V_l, \tag{1.7}$$

where $V_l = T_f V T_{-f}$ is the potential V translated by f along the negative x_1-axis, and $V_r = \mathscr{R} T_f V T_{-f} \mathscr{R}$ is the reflection of V_l about $x_1 = 0$.

3. In the field-theoretic case, $V \to \infty$ at ∞, which makes convergence proofs easier; see Reed and Simon [22, Vol. IV]. Formulae for the eigenvalue gaps carry over from this paper without change, though they may be more difficult to evaluate.

Definition (1.8). For an unperturbed Hamiltonian

$$h = -\Delta + V(\mathbf{x}),$$ (1.9)

define

$$H_f = -\Delta + W_f(\mathbf{x}),$$ (1.10)

with W_f as in (1.7), as the related double-well Hamiltonian.

Remark. For $V \in \mathscr{V}$, both (1.9) and (1.10) are bounded below and have $\sigma_{\text{ess}} = \mathbb{R}^+$.

Theorem (1.11). *Suppose that $e < 0$ is a nondegenerate (see Remark 2, below) eigenvalue of h, $V \in \mathscr{V}$, and e is isolated from the rest of the spectrum by a distance $> d$. For all $\varepsilon > 0$, there exists f_0 such that if $f > f_0$, then there are exactly two eigenvalues of H_f nearer to e than d, and as $f \to \infty$ they converge to e.*

A companion to this theorem gives an estimate of the eigenfunctions in the L^2 sense.

Theorem (1.12). *For $V \in \mathscr{V}_s$, the eigenfunctions $\Psi_\pm$ associated with the two eigenvalues $E_\pm$ approaching e by Theorem (1.11) can be normalized so as to satisfy*

$$H_f \Psi_\pm(f) = E_\pm \Psi_\pm(f);$$
$$\mathscr{R} \Psi_\pm = \pm \Psi_\pm;$$ (1.13)
$$\|\Psi_\pm\| = 1;$$
$$\|\Psi_\pm - (T_f \Phi \pm \mathscr{R} T_f \Phi)/\sqrt{2}\| \to 0,$$

where

$$h\Phi = e\Phi;$$
$$\|\Phi\| = 1$$ (1.14)

(when unindexed, $\|\dots\| = \|\dots\|_2$).

Remarks. 1. These theorems show that the LCAO method of chemistry, viz., approximating eigenfunctions of H_f with linear combinations of those of h as in (1.13), while not generally numerically accurate, as noted above, is at least valid in an asymptotic sense.

2. Analogous theorems hold for eigenvalues degenerate because of a symmetry such as under rotation about the x_1 axis, by restriction to the appropriate subspace.

3. It would be possible to say something about the size of f_0 and the rate of convergence in (1.11) for specific choices of V.

4. See the references for a proof of Theorem (1.11). The easy part is to show the existence of two eigenvalues near e; this follows from a variational estimate with

LCAO eigenfunctions and Weinhold's lemma (see [18]). The hard part is the absence of extraneous eigenvalues.

The proof of Theorem (1.12) is a simple consequence of Kato's generalization of Temple's inequality (see [23–25]), once the convergence has been controlled in its general outlines by Theorem (1.11). Since this theorem is also used later, it is stated here:

Theorem (1.15). *Let A be self-adjoint and $\Psi \in D(A)$, $\|\Psi\| = 1$. Suppose that E is the only eigenvalue of A in an interval $\alpha < E < \beta$, and let $\eta = (\Psi | A\Psi)$ and $\varepsilon^2 = \|[A - \eta]\Psi\|^2 = \|A\Psi\|^2 - \eta^2$. If $\varepsilon^2 < (\beta - \eta)(\eta - \alpha)$, then*

$$\eta - \varepsilon^2/[\beta - \eta] \leq E \leq \eta + \varepsilon^2/[\eta - \alpha]. \tag{1.16}$$

Remark. The error in the upper bound depends on the *lower* isolation distance and vice versa.

Corollary (1.17). *Let $F(f)$ be a trial function for H_f, i.e., $F(f) \in D(H_f)$ and $\|F(f)\| = 1$. If $\|[H_f - e]F(f)\| \to 0$, then one eigenvalue E of H_f satisfies*

$$|E - e - (F(f)|[H_f - e]F(f))| \leq \mathrm{const}\,\|[H_f - e]F(f)\|^2$$

for $f > f_0$.

Proof. $\lim\limits_{f \to \infty} (F(f)|H_f F(f)) \to e$, which is isolated from the rest of the spectrum of H_f by at least d for f large enough. Using $F(f)$ as the trial function Ψ of Theorem (1.15), eventually $\varepsilon^2 < (\beta - \eta)(\eta - \alpha)$, for α, $\beta = e \pm$ something a little greater than d, and the corollary follows immediately (most easily seen with $A = H_f - e$).   □

The following variant of the Eckart bound is proved in [25]:

Proposition (1.18). *Let A be self-adjoint with eigenvalue λ isolated from the rest of the spectrum by a distance d, and let P be the associated eigenprojection. If*

$$\|[H - \lambda]\zeta\| < d, \|\zeta\| = 1,$$

then

$$1 \geq \|P\zeta\|^2 \geq 1 - \|[H - \lambda]\zeta\|^2/d^2. \tag{1.19}$$

Corollary. *Theorem (1.12).*

Proof. Use Corollary (1.17) with

$$F_\pm = N_f(T_f\Phi \pm T_{-f}\mathscr{R}\Phi), \tag{1.20}$$

where $N_f = 1/\|T_f\Phi \pm T_{-f}\mathscr{R}\Phi\|$ clearly $\to 1/\sqrt{2}$. The assumptions guarantee that $F_\pm \in D(H_f)$, and it is easy to calculate that

$$[H_f - e]F_\pm = N_f(\mathscr{R} \pm 1)T_f V T_{-2f}\mathscr{R}\Phi$$
$$= N_f(V_r\Phi_l \pm V_l\Phi_r), \tag{1.21}$$

where $\Phi_l = T_f\Phi$ is the left LCAO contribution to the eigenfunction and $\Phi_r = T_{-f}\mathscr{R}\Phi$ is the right contribution. Since $\mathscr{R}\Phi \in D(-\Delta + 1)$, there exists $g \in L^2(\mathbb{R}^n)$

such that

$$\mathcal{R}\Phi = (-\varDelta + 1)^{-1} g,$$

and

$$T_{-2f}\mathcal{R}\Phi = (-\varDelta + 1)^{-1} T_{-2f} g.$$

Since $T_{-2f}g \to 0$ weakly as $f \to \infty$ and $V(-\varDelta + 1)^{-1}$ is compact,

$$\begin{aligned}
\|[H_f - e] F_\pm\| &\leq 2N_f \|T_f V(-\varDelta+1)^{-1} T_{-2f} g\| \\
&= 2N_f \|V(-\varDelta+1)^{-1} T_{-2f} g\| \\
&\to 0.
\end{aligned} \tag{1.20}$$

The previous corollary then shows that

$$|E_\pm - e - (F_\pm|[H_f - e] F_\pm)| = O(\|[H_f - e] F_\pm\|^2),$$

so (1.13) follows from the orthogonality of $F_\pm$ and Proposition (1.18). $\quad\square$

II. Eigenvalue Gaps and Eigenfunction Asymptotics

This section will present two different methods for estimating the eigenvalue gap. With both methods, an estimate of the gap is equivalent to a certain asymptotic estimate of the behavior of the eigenfunctions at large distances from a well. The details of the asymptotics needed are somewhat different for the two methods, and also somewhat different from the asymptotic estimates needed in [2, 26]. The twin methods appear mixed together in an embryonic form in [11], where an approximate, rigorous formula for the gaps between g and u energies of H_2^+ is derived, and evaluated with a nonrigorous, but correct, asymptotic functional approximation. In fact, one of these methods leads quite readily to an exact formula for the gaps for general double wells.

Theorem (2.1). *Define H_f as in (1.10) for $V \in \mathcal{V}_s$. Consider any two eigenvalues $E_\pm$ for which the eigenfunctions $\Psi_\pm$ are respectively even and odd under $\mathcal{R}$. Define the operator S such that*

$$[Sf](\mathbf{x}) \equiv \begin{cases} f(\mathbf{x}), & x_1 > 0 \\ -f(\mathbf{x}), & x_1 < 0. \end{cases} \tag{2.2}$$

If $(S\Psi_-|\Psi_+) \neq 0$, then

$$E_- - E_+ = \frac{2}{(S\Psi_-|\Psi_+)} \int \Psi_+(0, x_2, \ldots) \partial \bar{\Psi}_-(0, x_2, \ldots)/\partial x_1 dx_2 \ldots dx_n. \tag{2.3}$$

Remarks. 1. The conditions on the potential can be considerably relaxed; little more than $V \in C^m$ for the appropriate m in a neighborhood of $\{x_1 = 0\}$ and the absence of strong local singularities is required. For example, V may be allowed to grow as $|\mathbf{x}| \to \infty$.

2. Formula (2.3) is not restricted to natural pairs of geminate eigenvalues, which exist in a limit by Theorems (1.11) and (1.12), but to any pair of a symmetric

and an antisymmetric state. However, in the general case both the numerator and the denominator of (2.3) are typically small and thus it says little about $E_- - E_+$; whereas if the two eigenvalues are a geminate pair, then $(S\Psi_-|\Psi_+) \simeq \|\Psi_-\| \|\Psi_+\|$, which is normalized to 1.

3. It was only for convenience of reference that the potential was written in the same form as in (1.7). Theorem (2.1) applies to any such bilaterally symmetric potential, and has nothing to do with the parameter f.

4. Physically, the right side of (2.3) is a current. Therefore it makes precise the statement that nearness of eigenvalues is related to small likelihood of tunneling between the wells according to the uncertainty principle.

Proof. Note that

$$[H_f - E_-]\,\Psi_+ = [E_+ - E_-]\,\Psi_+,$$

so, taking an inner product with $S\Psi_-$,

$$E_- - E_+ = (S\Psi_-|[E_- - H_f]\,\Psi_+)/(S\Psi_-|\Psi_+).$$

Therefore, by using the symmetries of the eigenfunctions and Green's formula, one gets (2.3) from:

$$\begin{aligned}
(S\Psi_-|[E_- - H_f]\,\Psi_+) &= 2 \int\limits_{x_1 \geqq 0} \bar{\Psi}_- [E_- + \Delta - W]\,\Psi_+\, dx_1 dx_2 ... dx_n \\
&= 2 \int\limits_{x_1 \geqq 0} \overline{[(E_- + \Delta - W)\,\Psi_-]}\,\Psi_+\, dx_1 dx_2 ... dx_n \\
&\quad + 2 \int\limits_{x_1 = 0} (\Psi_+ \partial\bar{\Psi}_-/\partial x_1 - \bar{\Psi}_- \partial\Psi_+/\partial x_1)\, dx_2 dx_3 ... dx_n \\
&= 2 \int\limits_{\{x_1 = 0\}} \Psi_+ \frac{\partial\Psi_-}{\partial x_1}\, dx_2 ... dx_n.
\end{aligned} \tag{2.4}$$

The use of Green's formula is justified as follows: The Schrödinger regularity theorem guarantees that $\Psi_\pm \in C^2$ in a neighborhood of $\{x_1 = 0\}$, so $\Psi_\pm = A_\pm + B_\pm$, where $A_\pm$ is C^2 and supported near $\{x_1 = 0\}$ and $B_\pm \in D(H_f)$ and vanishes near $\{x_1 = 0\}$. Thus the integral of (2.4) consists of four parts, and Green's formula obviously applies to each of them assuming the integrals are finite. The boundary integral will be finite as a consequence of general pointwise bounds on $\Psi_\pm$ and $\partial\Psi_\pm/\partial x_1$, which are in a sense the subject of much of this paper: (2.7), (2.15), (2.16), (5.5), (5.7). $\square$

The alternative argument that reduces the problem of the eigenvalue gap to eigenfunction asymptotics is based on Temple's inequality (1.15). This shows that accurate trial functions lead to accurate estimates of eigenvalues, and gives useful bounds on the errors. In order to apply this argument, it is necessary to first get some information about exponential fall-off of eigenfunctions. Much has been done in this field, and the results given below overlap earlier ones to a great extent, especially for $n = 3$. They are proved here because they are tailor-made for the subject of this article, and so that the exposition is self-contained. An early bound of the type of Lemma (2.6) is due to Slaggie and Wichmann [27]. See also the work

of Shnol' quoted in Glazman, [28], and [29, 22, 30, 31]. The quickest way to the result uses a subharmonic comparison theorem of Deift et al. [30]:

Lemma (2.5). *Suppose that S is a closed set, $V \geqq W \geqq 0$ on $\overline{\mathbb{R}^n \backslash S}$, and f and g are continuous and $\Delta|g| \geqq V|g|$ and $\Delta|f| \leqq W|f|$ (in the distributional sense). If $|g| \leqq |f|$ on ∂S and f and $g \to 0$ as $x \to \infty$, then $|g| \leqq |f|$ on $\mathbb{R}^n \backslash S$.*

Lemma (2.6). *Let h, e, Φ, etc. be as in (1.9)–(1.14), and suppose that $V \in \mathscr{V}$ is compactly supported. Then there exists a constant $C < \infty$ such that*

$$|\Phi(\mathbf{x})| \leqq CG_0(\mathbf{x}; e), \tag{2.7}$$

where $(-\Delta - e)G_0(\mathbf{x}; e) = \delta^n(\mathbf{x})$.

Proof. It is known [22, 32] that under these conditions on V the eigenfunction is bounded, $\|\Phi\|_\infty < \infty$, so the bound (2.7) only needs to be shown for $\mathbf{x} \notin K = \{\mathbf{x} : \operatorname{dist}(\mathbf{x}, \operatorname{supp} V) \leqq 1\}$. This follows immediately from Lemma (2.5) and Kato's inequality, because G_0 and Φ solve the same equation on the complement of K. Since elliptic regularity makes Φ continuous and bounded on ∂K, C may be chosen large enough that CG_0 dominates Φ there (G_0 is strictly positive). $\square$

The simplest double-well problem to analyze has two symmetric, compactly supported wells. The following theorem will seem familiar in chemical circles.

Theorem (2.8). *Let $V \in \mathscr{V}$ be supported in a compact set K, and define h, H_f, etc. as before. Then*

$$E_\pm = e \pm 2N_f^2(\Phi|VT_{-2f}\mathscr{R}\Phi) + O(G_0^2(2f; e)); \tag{2.9}$$

and therefore

$$E_- - E_+ = -4N_f^2(\Phi|VT_{-2f}\mathscr{R}\Phi) + O(G_0^2(2f; e)). \tag{2.10}$$

Note that $N_f \to 1/\sqrt{2}$, and

$$(\Phi|VT_{-2f}\mathscr{R}\Phi) = O(G_0(2f; e)) = o(f^{-n}). \tag{2.11}$$

$\forall n < \infty$, *so unless there is a miraculous cancellation in $(\Phi|VT_{-2f}\mathscr{R}\Phi)$, to leading order,*

$$E_- - E_+ \sim -2(\Phi|VT_{-2f}\mathscr{R}\Phi). \tag{2.12}$$

Remark. To leading order, E_+ is what perturbation theory would predict for the eigenvalue if the second well were treated as the perturbation of the first.

Proof. By (1.21),

$$\|(H_f - e)F_\pm\| = \|N_f(1 \pm \mathscr{R})T_f VT_{-2f}\mathscr{R}\Phi\|$$

$$\leqq 2N_f\|VT_{-2f}\mathscr{R}\Phi\|$$

$$\leqq 2N_f\|V\|_2 \sup_{x \in K}|T_{-2f}\mathscr{R}\Phi|.$$

By assumption $\|V\|_2 < \infty$, and by (2.7),

$$\sup_K |T_{-2f}\mathscr{R}\Phi| = O(G_0(2f; e)).$$

Temple's inequality (1.15) applied to the restriction of $H_f - e$ to the even and respectively odd subspace under $\mathscr{R}$ states that

$$E_{\pm} = (F_{\pm}|H_f F_{\pm}) + O(\|(H_f - e) F_{\pm}\|^2)$$

$$= (F_{\pm}|H_f F_{\pm}) + O(G_0^2(2f;e)), \qquad (2.13)$$

because the restriction makes the isolation distance of $E_{\pm}$ at least $O(1)$ in f. Then, from (1.19),

$$E_{\pm} = e + (F_{\pm}|(1 \pm \mathscr{R}) N_f T_f V T_{-2f} \mathscr{R}\Phi) + O(G_0^2(2f;e))$$

$$= e \pm 2N_f^2((T_f\Phi \pm T_{-f}\mathscr{R}\Phi)|T_f V T_{-2f}\mathscr{R}\Phi) + O(G_0^2(2f;e))$$

$$= e \pm 2N_f^2(\Phi|V T_{-2f}\mathscr{R}\Phi) + 2N_f^2(T_f\Phi|\mathscr{R}T_f V T_{-f}\mathscr{R}T_f\Phi)$$

$$\qquad + O(G_0^2(2f;e)),$$

and

$$(T_f\Phi|\mathscr{R}T_f V T_{-f}\mathscr{R}T_f\Phi) = (T_{2f}\Phi|\mathscr{R}V\mathscr{R}T_{2f}\Phi) = O(G_0^2(2f;e)),$$

yielding (2.11). (In the last line, $T_{-f}\mathscr{R} = \mathscr{R}T_f$ was used.) $\quad\square$

For comparison, a weaker form of (2.11) will be derived using the first method, Theorem (2.1). For this purpose it is necessary to modify Lemma (2.6) to show exponential fall-off of eigenfunctions away from double wells.

Lemma (2.14). *Let V be as in Theorem (2.9), and let $H_f \Psi_{\pm} = E_{\pm} \Psi_{\pm}$. Then there exists $C < \infty$ independent of f (but conceivably depending on ε). such that if distance $(\mathbf{x}, K_2) \geqq \varepsilon > 0$, $K_2 \equiv K(f) \cup \mathscr{R}K(f)$, where $K(f) \equiv \{\mathbf{x} : \mathbf{x} + f\hat{\mathbf{e}}_1 \in K\}$ and $\mathscr{R}K(f)$ is the reflection of K through $\{x_1 = 0\}$, then*

$$|\Psi_{\pm}(\mathbf{x})| \leqq C \{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1; E_{\pm}) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1; E_{\pm})\} \qquad (2.15)$$

and

$$|\partial\Psi_{\pm}/\partial x_1| \leqq C \{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1; E_{\pm}) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1; E_{\pm})\} . \qquad (2.16)$$

Proof. These two estimates would follow from essentially the same proof as for (2.6) except for the independence of C on f, because $\Psi_{\pm}$ and $\partial\Psi_{\pm}/\partial x_1$ satisfy the same equation as do $G_0(\mathbf{x} \pm f\hat{\mathbf{e}}_1; E_{\pm})$ on the complement of K_2. The bound and the constancy in f, however, follow from the Lippmann-Schwinger equation for $\Psi_{\pm}$: Dropping the $\pm$ for convenience, the time-independent Schrödinger equation is equivalent for $V \in \mathscr{V}$ to:

$$\Psi(\mathbf{x}) = -\int G_0(\mathbf{x} - \mathbf{y}; E) W(\mathbf{y}) \Psi(\mathbf{y}) d^n y$$

$$= -\int_K G_0(\mathbf{x} - \mathbf{y}; E) W(\mathbf{y}) \Psi(\mathbf{y}) d^n y. \qquad (2.17)$$

The only singularity of $G_0(\mathbf{x} - \mathbf{y})$ is at $\mathbf{x} = \mathbf{y}$, and is not attained in the integral.

Therefore,

$$|\Psi(x)| \leq \sup_{y \in K_2} |G(\mathbf{x} - \mathbf{y}; E)| \, \|W\Psi\|_1$$

$$\leq 2 \left[\sup_{y \in K(f)} G_0(\mathbf{x} - \mathbf{y}; E) + \sup_{y \in \mathscr{R}K(f)} G_0(\mathbf{x} - \mathbf{y}; f) \right] \|V\|_2$$

$$\leq C \{ G_0(\mathbf{x} + f\hat{\mathbf{e}}_1; E) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1; E) \},$$

giving (2.15), because the subharmonic comparison Lemma (2.5) allows $G_0(\mathbf{x} - \mathbf{y})$ to be dominated by $G_0(\mathbf{x})$, which solves the same equation away from K and 0. The other bound follows similarly from the differentiated Lippmann-Schwinger equation,

$$\partial \Psi(\mathbf{x})/\partial x_1 = - \int \partial G_0(\mathbf{x} - \mathbf{y}; E)/\partial x_1 W(\mathbf{y}) \Psi(\mathbf{y}) d^n y, \qquad (2.18)$$

which is justified for Ψ by elliptic regularity outside of K_2. Thus

$$|\Psi(\mathbf{x})/\partial x_1| \leq \left[\sup_{y \in K(f)} |\partial G_0(\mathbf{x} - \mathbf{y}; E)/\partial x_1| + \sup_{y \in \mathscr{R}K(f)} |\partial G_0(\mathbf{x} - \mathbf{y}; f)/\partial x_1| \right] \|W\|_2$$

$$\leq C \{ G_0(\mathbf{x} + f\hat{\mathbf{e}}_1; E) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1; E) \},$$

again by subharmonic comparison by (2.5) and the fact that G_0 and $\partial G_0/\partial x_1$ satisfy the same equation away from their singularities. $\square$

These a priori bounds on the fall-off of the eigenfunctions allow bounds on the eigenvalue gap to be derived from (2.3) even if nothing else is known about $\Psi_\pm$. For large $|\mathbf{x}|$,

$$G_0(\mathbf{x}; \lambda) \sim \text{const} |\mathbf{x}|^{-(n-1)/2} \exp(-\sqrt{-\lambda}|\mathbf{x}|) \qquad (2.19)$$

[33]. If $n = 1$, then (2.3) contains no integral, and states that

$$E_- - E_+ \leq 4C^2 G_0(f; E_-) G_0(f; E_+) = O(\exp(-(\sqrt{-E_-} + \sqrt{-E_+})f)), \quad (2.20)$$

and the same estimate follows when $n \geq 2$, because

$$E_- - E_+ \leq \text{const} \int_{\{x_1 = f\}} |\mathbf{x}|^{-n+1} \exp(-(\sqrt{-E_-} + \sqrt{-E_+})|\mathbf{x}|) d^{n-1} x$$

$$\leq \text{const}' \int_0^\infty d\varrho \, \varrho^{n-2} \exp(-(\sqrt{-E_-} + \sqrt{-E_+})$$

$$\cdot \sqrt{\varrho^2 + f^2})/(\varrho^2 + f^2)^{(n-1)/2}, \qquad (2.21)$$

by transformation to polar coordinates, and the integral of (2.21) can be shown to be $O(\exp(-(\sqrt{-E_-} + \sqrt{-E_+})f)$.

An advantage of Temple's inequality is that strict symmetry under $\mathscr{R}$ is not required. Consider two single-well Hamiltonians h_1 and h_2, with $|V_{1,2}|$ bounded and of compact support, and such that h_1 and h_2 have a common, isolated, nondegenerate eigenvalue e:

$$h_1 \Phi_1 = e \Phi_1$$

$$h_2 \Phi_2 = e \Phi_2.$$

Define $L_f = -\Delta + T_{-f} V_1 T_f + T_f V_2 T_{-f} = -\Delta + V_r + V_l$, the Hamiltonian having the sum of the two single-well potentials after translation by $\pm f$ in the x_1-direction. Then, as before, for f large enough L_f has exactly two eigenvalues near e, which converge to e as $f \to \infty$. Moreover, the asymptotics of the eigenvalue gap are similar to before:

Theorem (2.22). *Let $E_\pm$ be the two eigenvalues associated with e, $E_\pm(f) \to e$, $E_- \geq E_+$, and*

$$L_f \Psi_\pm = E_\pm \Psi_\pm .$$

Suppose that

$$|(\Phi_l | V_r \Phi_l)| + |(\Phi_r | V_l \Phi_r)| = o(f^n \{(\Phi_r | V_r \Phi_l) + (\Phi_l | V_l \Phi_r)\})$$

$$\to 0 \tag{2.23}$$

for all $n < \infty$. Then

$$E_- - E_+ = -\{(\Phi_r | V_r \Phi_l) + (\Phi_l | V_l \Phi_r)\}(1 + o(f^{-n})) \tag{2.24}$$

for all $n < \infty$.

Remarks. 1. The restriction to bounded V is for convenience (but compact support is essential).

2. The conditions (2.23) on estimates involving the unperturbed problem are typically true and easy to verify. The right side is ordinarily $O(\exp(-2\sqrt{-e}\,f))$ and the left side is ordinarily $O(\exp(-4\sqrt{-e}\,f))$. There could be difficulties if $\Phi_{r,l}$ has a nodal surface along the x_1-axis or under peculiar circumstances leading to a cancellation on the right side.

Proof. The general fact of convergence is again left to the references. Instead of $F_\pm$, consider the set of trial functions of the form

$$F_\pm^\alpha = (\sqrt{\alpha} \Phi_l \pm \sqrt{1-\alpha}\, \Phi_r) N_{f,\alpha,\pm} ,$$

$$0 \leq \alpha \leq 1, \Phi_l = T_f \Phi_2, \quad \text{and} \quad \Phi_r = T_{-f} \Phi_1 .$$

It is straightforward to see that

$$[H - e] F_\pm^\alpha = N_{f,\alpha,\pm} (\sqrt{\alpha} V_r \Phi_l \pm \sqrt{1-\alpha}\, V_l \Phi_r), \tag{2.25}$$

and if the normalization is such that $\|F_\pm^\alpha\| = 1$, then $\|[H - e] F_\pm^\alpha\| \to 0$. Recalling the remark to Theorem (1.15), Temple's inequality gives a better upper (respectively lower) bound to E_+ (resp. E_-) than its lower (resp. upper) bound; for any α,

$$E_- - e \geq (F_-^\alpha | [H - e] F_-^\alpha) - O(\|[H - e] F_-^\alpha\|^2)$$

$$= -N_{f,\alpha,-}^2 \sqrt{\alpha - \alpha^2} \{(\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l)\}$$

$$+ N_{f,\alpha,-}^2 \{\alpha(\Phi_l | V_r \Phi_l) + (1 - \alpha)(\Phi_r | V_l \Phi_r)\} - O(\|[H - e] F_-^\alpha\|^2)$$

$$> +N_{f,\alpha,+}^2 \sqrt{\alpha - \alpha^2} \{(\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l)\}$$

$$+ N_{f,\alpha,+}^2 \{\alpha(\Phi_l | V_r \Phi_l) + (1 - \alpha)(\Phi_r | V_l \Phi_r)\}$$

$$+ O(\|[H - e] F_+^\alpha\|^2) \geq E_+ - e . \tag{2.26}$$

$$\geq E_+ - e .$$

Note that since Φ_r and Φ_l fall off exponentially away from V_r and V_l, the normalization is $N_{f,\alpha,+} = N_{f,\alpha,-} + o(f^{-n}) = 1 + o(f^{-n})$ for all n, so it will henceforth be set to 1 and the difference will be absorbed into the error term.

At the same time, there exists a particular value of α, say $\alpha = \beta$, for which F_+^β is orthogonal to the exact higher eigenfunction Ψ_-, so the complementary bound for E_+ is improved; consider F_+^β a trial function for $[H - e][1 - P_-]$, where P_- is the projection onto Ψ_-, so now E_+ is isolated by a distance independent of f (unlike $E_- - E_+$). Then

$$
\begin{aligned}
E_+ - e &\geq \left[\sqrt{\beta - \beta^2} \left\{ (\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l) \right\} (1 + o(f^{-n})) \right. \\
&\quad + \left\{ \beta (\Phi_l | V_r \Phi_l) + (1 - \beta)(\Phi_r | V_l \Phi_r) \right\} (1 + o(f^{-n})) \right] \\
&\quad - O(\| [H - e] F_-^\beta \|^2) \\
&\geq \min_\alpha [\ldots] - O\left(\max_\alpha \| [H - e] F_-^\alpha \|^2 \right) \\
&= \tfrac{1}{2} \left\{ (\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l) \right\} (1 + o(f^{-n})) \\
&\quad + \tfrac{1}{2} \left\{ (\Phi_l | V_r \Phi_l) + (\Phi_r | V_l \Phi_r) \right\} (1 + o(f^{-n})),
\end{aligned}
\tag{2.27}
$$

because of (2.23), (2.25), and because

$$
\| V_r \Phi_l \|^2 \leq \| V_1 \|_\infty (\Phi_l | V_r \Phi_l),
$$

and similarly for $V_l \Phi_r$. The minimum is taken at

$$
\alpha = \tfrac{1}{2} + O\left(\{ (\Phi_l | V_r \Phi_l) + (\Phi_r | V_l \Phi_r) \} / \{ (\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l) \} \right).
$$

Inequality (2.27) coupled with (2.26) for $\alpha = 1/2$ implies that

$$
E_+ = e + \tfrac{1}{2} \left\{ (\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l) \right\} (1 + o(f^{-n})),
$$

for all n, and the analogous argument for E_- gives

$$
E_- = e - \tfrac{1}{2} \left\{ (\Phi_l | V_l \Phi_r) + (\Phi_r | V_r \Phi_l) \right\} (1 + o(f^{-n})),
$$

so subtraction yields (2.24).   □

It is clear that the proof actually gives an exponentially small error estimate that would not be difficult to write down.

Note. Sigal and Klaus have separately pointed out in private communications that (2.12), etc. can also be derived with the perturbation argument of Klaus and Simon [34]. Since Temple's inequality is one of the ways to derive perturbation theory for self-adjoint operators [24], this is a closely related argument at a fundamental level.

III. The Anharmonic Oscillator in One Dimension

This is an important example, and has already received a great deal of attention as cited in the introduction; in particular a leading-order asymptotic formula for the eigenvalue gap has been proved in [2]. Hence, in recovering the same result using

the twin methods of this article some niceties will be pretermitted. The standard double-well anharmonic oscillator may be written

$$-d^2/dx^2 + x^2 - 2\beta x^3 + \beta^2 x^4 = -d^2/dx^2 + x^2(1-\beta x)^2$$
$$= -d^2/dx^2 + 1/16\beta^2 - \tfrac{1}{2}(x - 1/2\beta)^2 + \beta^2(x - 1/2\beta)^4, \tag{3.1}$$

as an operator on $L^2(\mathbb{R})$. It is equivalent to study

$$-d^2/dy^2 + W(y;\beta) \equiv -d^2/dy^2 - y^2/2 + \beta^2 y^4. \tag{3.2}$$

Let $\sigma_\beta(y)$ be a real-valued eigenfunction of

$$-d^2/dy^2 + U(y;\beta) \equiv -d^2/dy^2 + W(y;\beta)\chi_+, \tag{3.3}$$

where $\chi_+ = \chi_{[0,\infty)}(x) = 1$ if $x \geq 0$ and otherwise 0. The eigenvalue corresponding to σ_β is $\tilde{E}(\beta) \to 2n + 1 - 1/16\beta^2$. As before, it is known that (3.2) has geminate pairs of eigenvalues $E_\pm$, and $E_\pm + 1/16\beta^2$ coalesce to $2n+1$ as $\beta \to 0$. The gap $E_- - E_+$ will first be estimated using Temple's inequality: Note that

$$[H(\beta) - \tilde{E}] N_\beta(\sigma_\beta \pm \mathscr{R}\sigma_\beta) = N_\beta(\sigma_\beta(\mathscr{R}U - \tilde{E})\chi_+ + (\mathscr{R}\sigma_\beta)(U - \tilde{E})\mathscr{R}\chi_+),$$

where N_β is normalization and $\to 1/\sqrt{2}$. If $y > 0$, then σ_β satisfies a free Schrödinger equation, so clearly

$$\sigma_\beta(y) = \sigma_\beta(0)\exp(-\sqrt{-\tilde{E}}\, y), \tag{3.4}$$

and by Temple's inequality (1.15) using $N_\beta(\sigma_\beta \pm \mathscr{R}\sigma_\beta)$ as the trial function,

$$E_\pm = \tilde{E} + N_\beta^2(\sigma_\beta \pm \sigma_\beta|[\mathscr{R}U - \tilde{E}]\chi_+\sigma_\beta \pm [U - \tilde{E}]\mathscr{R}\chi_+\sigma_\beta) + \dots$$
$$= \tilde{E} + N_\beta^2\{2(\sigma_\beta|[\mathscr{R}U - \tilde{E}]\chi_+\sigma_\beta) \pm 2(\mathscr{R}\sigma_\beta|[\mathscr{R}U - \tilde{E}]\chi_+\sigma_\beta)\} + \dots,$$

where $\dots$ means that the other terms are $o(f^{-n})$ times the smallest one written. The exponential smallness of the dropped terms follows from (3.4).

$$E_- - E_+ = -4N_\beta^2(\mathscr{R}\sigma_\beta|[\mathscr{R}U - E]\chi_+\sigma_\beta) + \dots$$
$$= -4N_\beta^2((d^2/dy^2)\mathscr{R}\sigma_\beta|\chi_+\sigma_\beta) + \dots$$
$$= 4N_\beta^2\{(1/16\beta^2 + \tilde{E})(\mathscr{R}\sigma_\beta|\chi_+\sigma_\beta) + 2\sqrt{-\tilde{E}}\,\sigma_\beta^2(0) + \dots$$
$$= (\sigma_\beta^2(0)/\beta)(1 + O(\beta^2))$$

by integration by parts. The task is thus to estimate $\sigma_\beta(0)$. As can be proved following [26], a good pointwise estimate of $\sigma_\beta(y)$ is:

$$\sigma_\beta(y) = \begin{cases} CD_{-(\tilde{E}-1)/2}(\sqrt{2}x) = CD_{-(\tilde{E}-1)/2}(\sqrt{2}(y + 1/2\beta)), & |y - 1/2\beta| < \beta^{-\alpha} \\ C'(W(y) - \tilde{E})^{-1/4}\exp\left(-\int_{-1/2\beta} y\,\mathrm{Re}(W(z) - \tilde{E})^{1/2}dz\right), & y - 1/2\beta > \beta^{-\alpha} \end{cases}$$

for some $\alpha \in (0, 1/2)$ and constants C and C' [and $D_a(z)$ is a parabolic cylinder function]. In words, $\sigma_\beta(y)$ is roughly a harmonic-oscillator function where the perturbation is small and is given by WKB elsewhere. The constants can be determined by looking up the normalization of harmonic oscillator eigenfunctions [35] and by asymptotically matching the functions at $x = \beta^{-\alpha}$, at least to leading

order. Using formulae from [33] and the integral,

$$\int_{-1/2\beta}^{-1/2\beta+\beta^{-\alpha}} \mathrm{Re}(W(y)-E)^{1/2}\,dy = \int_{0}^{\beta^{-\alpha}} \mathrm{Re}(x^2-(2n+1))^{1/2}\,dx + O(\beta^{\gamma})$$

$$= \tfrac{1}{2}[\beta^{-\alpha}(\beta^{-2\alpha}-2n-1)^{1/2}-(2n+1)\ln(\beta^{-\alpha}+(\beta^{-2\alpha}-2n-1)^{1/2}]$$

$$+ \ln(2n+1)^{(2n+1)/4} + O(\beta^{\gamma}),\ \gamma>0,$$

shows that for $y>-1/2\beta+\beta^{-\alpha}$,

$$\sigma_{\beta}(y) = (\pi^{-1/4}2^{-1/4}/\sqrt{n!})(2e/(2n+1))^{-(2n+1)/4}2\beta^{1/2}$$

$$\cdot \exp\left(-2\int_{-1/2\beta}^{y} \mathrm{Re}(W(z)-2n-1)^{1/2}\,dz\right)(1+O(\beta^{\gamma})).$$

Therefore

$$E_{-}-E_{+} = \frac{2^{1-n}((2n+1)/e)^{(2n+1)/2}}{n!\sqrt{\pi}}$$

$$\cdot \exp\left(-2\int_{-1/2}^{0} \mathrm{Re}(W(y)-2n-1)^{1/2}\,dy\right)(1+O(\beta^{\gamma})), \qquad (3.5)$$

which agrees with [2].

The same result can be reached from Theorem (2.1), which in one dimension reduces to

$$E_{-}-E_{+} = 2\Psi_{+}(0)\,\Psi'_{-}(0)/(S\Psi_{-}|\Psi_{+}). \qquad (3.5)$$

Clearly, for a geminate pair $(S\Psi_{-}|\Psi_{+})\to 1$, and the problem is to estimate the eigenfunctions and their derivatives. The following fact simplifies the analysis somewhat:

Proposition (3.7). *Let*

$$\Phi_{n}(x) = (1/\pi^{1/2}2^{n}n!)^{1/2}H_{n}(x)\exp(-x^2/2), \qquad (3.8)$$

which is the n-th normalized harmonic-oscillator eigenfunction, i.e., $(-d^2/dx^2+x^2)\Phi_{n}=(2n+1)\Phi_{n}$. *Then the eigenfunctions* $\Psi_{\pm}(-1/2\beta, \beta)$ *and their derivatives* $\Psi'_{\pm}(-1/2\beta, \beta)$ *are continuous in β and*

$$\Psi_{\pm}(1/2\beta, \beta)\to\Phi_{n}(0),$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3.9)$

$$\Psi'_{\pm}(1/2\beta, \beta)\to\Phi'_{n}(0).$$

Proof Sketch. This is a known result except for minor details. It is convenient to think of $\Psi_{\pm}$ as an eigenfunction of (3.1) and therefore evaluated at the fixed point $x=0\Leftrightarrow y=-1/2\beta$. An eigenfunction must equal a function of β times the subdominant (dying) solution as $x\to-\infty$ of the ordinary differential equation it satisfies. It is known that this subdominant solution is entire in β (and also in E, regarded as a parameter) [36, 37] for fixed x. The same holds for the derivative, and the normalization is continuous, so the theorem follows.   □

Proposition (3.7) means that up to a correction that vanishes as $\beta \rightarrow 0$, the problem of estimating $\Psi_{\pm}(x)$ pointwise is the same as estimating solutions to the eigenvalue equation required (a) to be symmetric or antisymmetric about $x = 0$, which is the same as having a Neumann or Dirichlet boundary condition there; and (b) to have the same logarithmic derivative at $y = -1/2\beta$ as Φ_n has at $x = 0$, which also amounts to posing a Dirichlet or Neumann condition, depending on the parity of n, at $y = -1/2\beta$. But this is just a special case of the reduced problem of [26], so $\Psi_{+}(0)$ and $\Psi'_{-}(0)$ can be substituted for from there, which leads to (3.4) to leading order [cf. (1.5) of [26] and note that the normalization is different by a factor $(\sqrt{2})^2 = 2$].

IV. The Hydrogen Molecular Ion

This is another essentially one-dimensional problem, because of the separation in elliptic, or more exactly prolate ellipsoidal, coordinates. The simplest use of Temple's inequality would be to let the trial functions be LCAO, that is, combinations of hydrogen wave-functions. This choice of trial functions could be used to prove the coalescence of the eigenvalues as in Theorem (1.11), but fails to estimate the gap between g and u states, because of the long range of the Coulomb force. Though H_2^+ makes a simple theoretical model, it actually exists, and beams of it can be produced in the laboratory [38].

In natural units, the Hamiltonian is (1.10) on $L^2(\mathbb{R}^3)$ with

$$V(x) = -\alpha/|\mathbf{x}|, \quad \alpha > 0. \tag{4.1}$$

The eigenvalue equation $H_f \Psi = E \Psi$ is separable in prolate spheroidal coordinates, η, ξ, and φ, such that

$$x_1 = f \eta \xi$$

$$x_2 = f \sqrt{(1 - \eta^2)(\xi^2 - 1)} \cos\varphi \tag{4.2}$$

$$x_3 = f \sqrt{(1 - \eta^2)(\xi^2 - 1)} \sin\varphi;$$

$$-1 \leqq \eta \leqq 1, \quad 1 \leqq \xi < \infty, \quad 0 \leqq \varphi \leqq 2\pi \cong 0.$$

In these coordinates, $\Psi = \Lambda(\xi) S(\eta) \exp(im\varphi)$, where

$$\frac{d}{d\eta}(1 - \eta^2) dS/d\eta + (-pa + p^2(\eta^2 - 1) - m^2/(1 - \eta^2))S = 0 \tag{4.3}$$

and

$$\frac{d}{d\xi}(\xi^2 - 1) d\Lambda/d\xi + (pa - p^2(\xi^2 - 1) - m^2/(\xi^2 - 1) + 2\alpha f \xi)\Lambda = 0, \tag{4.4}$$

and $p^2 = -f^2 E$, $m \in \mathbb{Z}$, and the separation constant is written pa, with the benefit of hindsight. The solutions of (4.3) are studied special functions [39] known as oblate [sic] spheroidal wave functions, and the ones regular at $\eta = \pm 1$ are denoted $S_{mn}(-ip, \eta)$, $n \geqq m$. Equation (4.4) was studied in [15]. When written in elliptic

coordinates, (2.3) becomes

$$E_- - E_+$$

$$= 2 \cdot \frac{S_{mn}(-ip,0)f^{-1}S'_{mn+1}(-ip,0)(2\pi f^2 \int_1^\infty A(\xi,E_+)A(\xi,E_-)\xi^2 d\xi)}{2\pi f^3 \left\{ -\int_{-1}^0 + \int_0^1 \right\} d\eta\, S_{mn}(-ip,\eta) S_{mn+1}(-ip,\eta) \int_1^\infty (\xi^2-\eta^2) A(\xi,E_+)A(\xi,E_-) d\xi}$$

$$= \frac{S_{mn}(-ip,0) S'_{mn+1}(-ip,0)}{f^2 \int_0^1 d\eta \cdot \left\{ 1 - \eta^2 \dfrac{\int_1^\infty A(\xi,E_+)A(\xi,E_-) d\xi}{\int_1^\infty \xi^2 A(\xi,E_+)A(\xi,E_-) d\xi} \right\} S_{mn}(-ip,\eta) S_{mn+1}(-ip,\eta)}$$

$$n = m + 2k, k = 0, 1, 2, \dots . \tag{4.5}$$

Remarks. 1. Equation (4.5) is an exact formula, for all values of f including the physical value, in terms of studied functions. Previous formulae appear to be only asymptotic expansions for $f \to \infty$ [17]. (Note that S_{mk} has parity $(-1)^{k-m}$ and that in the limit $p \to \infty$ there is eigenvalue coalescence for the S's with n and $n+1$ [39].)

2. The denominator of (4.5) and the parameter $a(f)$, which has been suppressed, are continuous in f and approach constants as $f \to \infty$. Thus, up to normalization, the eigenvalue gap for H_2^+ is equivalent to a similar property of the oblate spherical harmonics. In fact, (4.3) is equivalent to a one-dimensional double-well equation of Schrödinger type, for with $S = (1-\eta^2)^{-1/2}\psi$ and $\lambda = p\eta$,

$$-\psi_{\lambda\lambda} + \{ (m^2-1)(1/(p-\lambda) + 1/(p+\lambda))^2/4 + 1 + a(1/(p-\lambda) + 1/(p+\lambda))/2 \} \psi = 0$$

$$(a < 0). \tag{4.6}$$

Let us evaluate (4.5) in the limit $f \to \infty$, to compare it with earlier literature. As $f \to \infty$,

$$a \to -(2(m+1)+4v) + \frac{2v(v+m+1)+m+1}{p} + \dots , \tag{4.7}$$

$$v = \begin{cases} (n-m)/2, & n-m \text{ even} \\ (n-m-1)/2, & n-m \text{ odd}; \end{cases}$$

and (up to a constant)

$$S_{mn}(-ip,\eta) \to \begin{cases} (1-\eta^2)^{m/2} \exp(-p(1-\eta)) L_v^{(m)}(2p(1-\eta)), & 0 \ll p\eta \leq p \\ (1-\eta^2)^{m/2} \exp(-p(1-\eta)) L_v^{(m)}(2p(1-\eta)) + (-1)^v(\eta \to -\eta), \eta \simeq 0, \end{cases}$$

$$\tag{4.8}$$

where $L_v^{(m)}$ is a Laguerre polynomial ([39], where $a = -\lambda_{mn}/p - p$).

The equation for A reduces in the limit to the analogous equation for the hydrogen-atom Hamiltonian separated in parabolic coordinates (as does the equation for S near either end point). Perturbation theory shows that the

convergence is in the L^2 sense, so to leading order both Λ's may be replaced by their limit in the integrals in (4.5). To be more specific, let $\Lambda = (\xi^2 - 1)^{-1/2}\phi$ and then change variables so that $\zeta = p(\xi - 1)$: then (4.4) becomes

$$-\phi_{\zeta\zeta} + \left\{ \frac{m^2 - 1}{4\zeta^2} [1/(1 + \zeta/2p)]^2 + 1 - \frac{1}{\zeta}\left(\frac{\alpha}{\sqrt{-E}}[(1 + \zeta/p)/(1 + \zeta/2p)]\right)\right.$$

$$\left. + \frac{a}{2}[1 + \zeta/2p]^{-1}\right\}\phi = 0,$$

$$\zeta \in \mathbb{R}^+. \tag{4.9}$$

As $f \to \infty$, all terms in square brackets $[\;] \to 1$, and (4.9) becomes Whittaker's equation, just as for hydrogen. Keeping terms to $O(1/f) = O(1/p)$,

$$-\phi_{\zeta\zeta} + \left\{\frac{m^2 - 1}{4\zeta^2} + b^2 - 2b\kappa/\zeta\right\}\phi + \frac{1}{p^2}P(p, \zeta)\phi = 0, \tag{4.10}$$

where P is a uniformly bounded perturbation, and

$$b = \sqrt{1 - (\alpha/2\sqrt{-E} + (m+1)/2 + \nu)/p}$$

and

$$\kappa = \frac{(\alpha/\sqrt{-E} - (m+1) - 2\nu + (2\nu(\nu + m + 1) + m + 1)/2p + (m^2 - 1)/4p)}{2b}$$

$$= \alpha/2\sqrt{-E} - (m+1)/2 - \nu + \alpha^2/8(-E)p + O(p^{-2}).$$

The solution $\phi = W_{\kappa,m/2}(2b\zeta)$ regular at infinity is also regular at 0, and hence an eigenfunction for (4.9), when $\kappa - (m+1)/2 = 0, 1, 2, \ldots$. In the limit, ϕ becomes [40]

$$(-1)^k k! (2\zeta)^{(1+m)/2} \exp(-\zeta)L_k^{(m)}(2\zeta) + \text{something } O\left(\frac{1}{p}\right) \text{ in the } L^2 \text{ sense}, \tag{4.11}$$

and $E \to -\alpha^2/4k^2$, $k = \nu + m + 1, \nu + m + 2, \ldots$. From the eigenvalue condition and (4.7), one finds that to $O(1/f)$,

$$E = -\alpha^2/4k^2 - \alpha/2f + \ldots, \tag{4.12}$$

after a little algebra.

By changing variables and scaling,

$$\frac{\displaystyle\int_1^\infty \Lambda(\xi, E_+)\Lambda(\xi, E_-)\,d\xi}{\displaystyle\int_1^\infty \xi^2 \Lambda(\xi, E_+)\Lambda(\xi, E_-)\,d\xi} \to \frac{\displaystyle\int_0^\infty d\zeta\,\phi^2(\zeta)/\zeta(\zeta + 2p)}{\displaystyle\int_0^\infty d\zeta\,\phi^2(\zeta)(1 + \zeta/p)^2/\zeta(\zeta + 2p)} \to 1.$$

Thus (4.5) becomes

$$E_- - E_+ \to S_{mn}(-ip, 0)S'_{mn+1}(-ip, 0)/f^2 \int_0^1 (1 - \eta^2)S_{mn}(-ip, \eta)S_{mn+1}(-ip, \eta)\,d\eta. \tag{4.13}$$

The denominator of this is

$$f^2 \int_0^1 (1-\eta^2) S_{mn}(-ip,\eta) S_{mn+1}(-ip,\eta)d\eta$$

$$\to f^2 \int_0^1 d\eta (1-\eta^2)^{m+1} e^{-2p(1-\eta)}(L_\nu^{(m)}(2p(1-\eta)))^2$$

$$= f^2 \int_0^p \left(\frac{\mu}{p}\left(2-\frac{\mu}{p}\right)\right)^{m+1} \exp(-2\mu)(L_\nu^{(m)}(2\mu))^2 \frac{1}{p} d\mu$$

$$\to (2^{m+1}/-E)p^{-m} \int_0^\infty \mu^{m+1} \exp(-2\mu)(L_\nu^{(m)}(2\mu))^2 d\mu$$

$$= (2^{m+1}/-E)p^{-m}(-1)^\nu \frac{\Gamma(1+m+\nu)}{\nu!2^{2+m}} \sum_{j=0}^\nu \binom{1}{\nu-j}(-1)^j\left(\frac{\Gamma(m+j+2)}{j!\Gamma(m+1)}\right)_2$$

$$F_1(-j,m+j+2,m+1;0)$$

$$\to \frac{2k^2}{\alpha^2} p^{-m}\left(\frac{(m+\nu)!}{\nu!}\right)^2 \frac{m+1}{m!}, \tag{4.14}$$

because of (4.12) and formulae in [33, 40]. From (4.8) and other formulae in [33, 40],

$$S_{m,n}(-ip,0)S'_{m,n+1}(-ip,0) \to 4p \exp(-2p)[L_\nu^{(m)}(2p)]^2$$

$$\to 4p \exp(-2p)(-2p)^{2\nu}/(\nu!)^2 .$$

Thus (4.5) becomes

$$E_- - E_+ \sim \frac{2^{2+2\nu}\alpha^2 m! p^{1+m+2\nu}}{k^2((m+\nu)!)^2(m+1)} \exp(-2p)$$

$$\sim \frac{2^{1-m}\alpha^3 m! f^{1+m+2\nu}}{k^{3+m+2\nu}((m+\nu)!)^2(m+1)} \exp(-2p)$$

$$\sim \frac{2^{1-m}\alpha^3 m! f^{1+m+2\nu}}{k^{3+m+2\nu}((m+\nu)!)^2(m+1)} \exp(-\alpha f/k - k). \tag{4.15}$$

(The tilde means that the ratio $\to 1$.)

This agrees with the asymptotic calculations of [17], who use different normalization and notation. For example, with the ground state, $m = \nu = 0$, $k = 1$, Eq. (4.15) reads

$$E_- - E_+ \sim 2\alpha^3 f \exp(-\alpha f - 1), \tag{4.16}$$

which converts to the leading term of their Eq. (46) with $\alpha = 2$, $R = 2f$, and an overall factor multiplying (4.16) by $1/2$, from the difference in normalization.

V. Double Wells in n Dimensions without Compact Support or Elliptic Symmetry

Two sorts of n-dimensional double-well Hamiltonians have been considered above, but each one had a special property that simplified the analysis. The hydrogen molecular ion has a separable eigenvalue equation, and is thus essentially a one-dimensional problem like the anharmonic oscillator. The efficacy of the theory of ordinary differential equations for one-dimensional problems

makes the analysis much easier than otherwise. On the other hand, with potentials V of compact support, asymptotic estimates are obtainable by comparison with the free Schrödinger equation. It will be shown in this section that similar comparison arguments can be made in more general cases, at the cost of some additional labor and some weakening of the results.

Temple's inequality becomes ineffectual unless the potential V falls off very fast. Recall the proof of Theorem (2.8). The task is to bound

$$\|(H_f - e) F_\pm\| = O(\|VT_{-2f}\mathscr{R}\Phi\|),$$

but if V is not compactly supported, then although the exponential fall-off of Φ makes $VT_{-2f}\mathscr{R}\Phi$ very small near $\mathbf{x} = 0$ (where V lives), it is only $O(V(2f\hat{\mathbf{e}}_1))$ near $\mathbf{x} = 2f\hat{\mathbf{e}}_1$ (where $T_{-2f}\mathscr{R}\Phi$ lives). Therefore the error estimates given by Temple's inequality for the first (or n-th) order perturbative correction to the eigenvalue swamps the eigenvalue gap. This difficulty was avoided for the anharmonic oscillator by looking to the ordinary differential equation, a tactic not available in general.

It is, however, possible to refine Lemma (2.14) for the case at hand, giving exponential fall-off for the actual eigenfunctions $\Psi_\pm$. The comparison Lemma (2.5) can be used to bound $|\Psi_\pm|$ and $|\partial\Psi_\pm/\partial x_1|$ by $\mathrm{const}\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm + \delta) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm + \delta)\}$ for any $\delta > 0$, providing that V falls off as $|\mathbf{x}| \to \infty$, but it is not immediately clear that the constant is independent of f. Thus it is first necessary to have a crude, f-independent bound on $\Psi_\pm$ and their derivatives, uniformly in $\mathbf{x}$. Kato [32] and Herbst and Sloan [41] have proved bounds of the right type. The first proposition of this section states the appropriate bound for the double-well eigenfunctions:

Proposition (5.1). *Let* $V \in \mathscr{V}$, *where* q *of Definition* (1.6) *is* $> n/2$ *if* $n \geq 4$. *Then, with* H_f, $\Psi_\pm$, *etc. defined as in Sect. 1,*

$$\|\Psi_\pm\|_\infty \leq C(n)\|\Psi_\pm\|_2 = C(n), \tag{5.2}$$

for a constant $C(n)$ *independent of* f.

Remarks. 1. One way to prove this is to use the Lippmann-Schwinger equation (2.17) and the Green-function estimates:

$$G_0(x, E) \in L^q(\mathbb{R}^n) \quad \text{for} \quad E < 0$$

and

$$1 \leq q \leq \infty, n = 1;$$
$$1 \leq q < \infty, n = 2; \tag{5.3}$$
$$1 \leq q < n/(n-2), n \geq 3,$$

and make repeated applications of Young's inequality.

2. It is not difficult to weaken the assumptions on V to membership in one L^q space, q as in Definition (1.6), in which case C depends on q, and if $q = n/2$, $n > 4$, then the bound (5.2) only holds for $\mathbf{x} - f\hat{\mathbf{e}}_1$ and $\mathbf{x} + f\hat{\mathbf{e}}_1 \notin B$, where B is some fixed

ball centered at $\mathbf{x} = 0$. Constants $C(n)$ or $C(q, n)$ could be computed in terms of L^p norms of G_0 and V.

Corollary (5.4). *Let* $V \in \mathscr{V}_s$. *Then for arbitrarily small, positive* δ, *and* $\mathbf{x}$ *outside balls (this phrase will be an abbreviation for the kind of restriction on* $\mathbf{x}$ *in the previous remark),*

$$|\Psi_\pm(\mathbf{x})| \leqq \text{const}\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm + \delta) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm + \delta)\}. \tag{5.5}$$

Proof. This follows directly from Proposition (5.1) and the comparison Lemma (2.5); Choose balls large enough that

$$|\Psi_\pm(\mathbf{x})| \leqq C(n) \tag{5.6}$$

and $|W(\mathbf{x})| < \delta$ for $\mathbf{x}$ outside them. Since $\Psi_\pm$ is bounded on the surfaces of the balls independently of f, it is dominated by a large enough constant times $\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm + \delta) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm + \delta)\}$ there, and hence everywhere outside the balls by Lemma (2.5). $\square$

Proposition (5.7). *Under the same conditions,*

$$|\partial\Psi_\pm(\mathbf{x})/\partial x_1| \leqq \text{const}\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm + \delta) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm + \delta)\}.$$

Proof. Unlike (2.16), this does not follow immediately from (2.5) as for $\Psi_\pm(\mathbf{x})$; $\partial\Psi_\pm/\partial x_1$ satisfies an inhomogeneous differential equation, with an extra term $\Psi_\pm \partial W/\partial x_1$. However, it follows from the differentiated Lippmann-Schwinger equation:

$$\partial\Psi_\pm/\partial x_1 = \int (\partial G_0(\mathbf{x} - \mathbf{y}, E)/\partial x_1) \, W(\mathbf{y}) \, \Psi_\pm(\mathbf{y}) \, d^n y$$

$$= \underset{\mathbf{y} \in \text{large balls} \equiv M}{\int} + \underset{|\mathbf{y} - \mathbf{x}| \leqq 1}{\int} + \underset{\text{other } \mathbf{y}}{\int}, \tag{5.8}$$

where the balls are large enough that W is bounded outside them. Suppose the distance from $\mathbf{x}$ to M is at least 1. Then

$$\left| \underset{\mathbf{y} \in M}{\int} (\partial G_0(\mathbf{x} - \mathbf{y}, E_\pm)/\partial x_1) \, W(\mathbf{y}) \, \Psi(\mathbf{y}) \, d^n y \right|$$

$$\leqq \|\chi_M W\|_2 \|\Psi_\pm\|_2 \underset{\mathbf{y} \in M}{\sup} |\partial G_0(\mathbf{x} - \mathbf{y}, E_\pm)/\partial x_1|$$

$$\leqq \text{const}\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm)\} \tag{5.9}$$

(where χ_M is the characteristic function of M); and

$$\left| \underset{|\mathbf{y} - \mathbf{x}| \leqq 1}{\int} (\partial G_0(\mathbf{x} - \mathbf{y}, E_\pm)/\partial x_1) \, W(\mathbf{y}) \, \Psi(\mathbf{y}) \, d^n y \right|$$

$$\leqq \|\partial G_0/\partial x_1\|_1 \underset{|\mathbf{y} - \mathbf{x}| \leqq 1}{\sup} |W(\mathbf{y})| \underset{|\mathbf{y} - \mathbf{x}| \leqq 1}{\sup} |\Psi_\pm(\mathbf{y})|$$

$$\leqq \text{const}\{G_0(\mathbf{x} + f\hat{\mathbf{e}}_1, E_\pm + \delta) + G_0(\mathbf{x} - f\hat{\mathbf{e}}_1, E_\pm + \delta)\}, \tag{5.10}$$

by (5.5) and the fact that for $|\mathbf{z}| \geqq 2$ there is a constant C such that $G_0(\mathbf{z}', E) \leqq C G_0(\mathbf{z}, E)$ for all $\mathbf{z}'$ satisfying $|\mathbf{z}' - \mathbf{z}| \leqq 1$.

For the remaining integral, note that for $\mathbf{z}$ away from zero, $G_0(\mathbf{z}, E+\delta)$ is essentially $\exp(-\sqrt{-E-\delta}\,|\mathbf{z}|)$, because the coefficient of the exponential part of G_0 varies as an inverse power of $|\mathbf{z}|$, and is easily dominated by a small change in δ. Likewise for $\partial G_0/\partial x_1$. So, from the triangle inequality,

$$|\mathbf{x} \pm f\hat{\mathbf{e}}_1| \leqq |\mathbf{x}-\mathbf{y}| + |\mathbf{y} \pm f\hat{\mathbf{e}}_1|$$

$$\Rightarrow \exp(-\sqrt{-E}\,|\mathbf{x}-\mathbf{y}|)\exp(-\sqrt{-E-\delta}\,|\mathbf{y} \pm f\hat{\mathbf{e}}_1|)$$

$$\leqq \exp(-\sqrt{-E-\delta}\,|\mathbf{x} \pm f\hat{\mathbf{e}}_1|)\exp(-\delta_1|\mathbf{x}-\mathbf{y}|), \qquad (5.11)$$

for $\delta_1 = \sqrt{-E} - \sqrt{-E-\delta}$;

which implies that

$$|\Psi(\mathbf{y})\partial G_0(\mathbf{x}-\mathbf{y}, E_\pm)/\partial x_1| \leqq \mathrm{const}\, G_0(\mathbf{x}-\mathbf{y}, -\delta_1^2)\{G_0(\mathbf{x}+f\hat{\mathbf{e}}_1, E_\pm +\delta)$$
$$+ G_0(\mathbf{x}-f\hat{\mathbf{e}}_1, E_\pm +\delta)\}. \qquad (5.12)$$

Thus the remaining integral is bounded by

$$\mathrm{const}\,\{G_0(\mathbf{x}+f\hat{\mathbf{e}}_1, E_\pm +\delta) + G_0(\mathbf{x}-f\hat{\mathbf{e}}_1, E_\pm +\delta)\} \int_{\text{other } \mathbf{y}} G_0(\mathbf{x}-\mathbf{y}, -\delta_1^2)|W(\mathbf{y})|\, d^n y$$

$$\leqq \mathrm{const}\,\delta\|G(\cdot, -\delta_1^2)\|_1\{G_0(\mathbf{x}+f\hat{\mathbf{e}}_1, E_\pm +\delta) + G_0(\mathbf{x}-f\hat{\mathbf{e}}_1, E_\pm +\delta)\},$$

which completes the proof. $\square$

A more careful analysis would show that δ may be set to 0 if V falls off sufficiently fast. In any event, once fall-off of this sort has been proved, it is straightforward to bound the eigenvalue gap, since

$$E_- - E_+ \leqq \mathrm{const}\left|\int_{\{x_1 = 0\}} \Psi_+(\mathbf{x})\,\partial\Psi_-(\mathbf{x})/\partial x_1\, d^{n-1}x\right|$$

$$\leqq \mathrm{const}\int_{\{x_1 = 0\}} G_0^2(\mathbf{x}+f\hat{\mathbf{e}}_1, e+\delta)\, d^{n-1}x$$

$$= O(\exp(-2\sqrt{-e-\delta}\,f)), \qquad n=1,$$

and otherwise

$$\leqq \mathrm{const}\int_0^\infty \varrho^{n-2} f^{1-n}\exp(-2\sqrt{-e-\delta}\,\sqrt{f^2+\varrho^2})\, d\varrho$$

$$= O(f^{1-n}\exp(-2\sqrt{-e-\delta}\,f)). \qquad (5.13)$$

(These constants, which are of course not all the same, could be made explicit in terms of the various norms of V and G_0. They are complicated unless V is specified more narrowly.)

VI. Conclusion

A number of related facts about geminate pairs of eigenvalues and eigenfunctions of double-well Hamiltonians have been proved, principally with the goal of deriving and evaluating formulae for the differences of the eigenvalues. The asymptotics of these gaps are simply proportional to certain asymptotics of the

eigenfunctions; this is important because solutions of differential equations have a rich functional structure, from which it is possible to extract a great deal of information. At the risk of making this article as tedious as a twice-told tale, I have used two different, but often intertwined, analytical aids to spin out the theory of geminate eigenvalues; for the strengths of the two tools are complementary, and it is only with both that the theory is comprehensive enough.

There remain a few gaps and unresolved related issues. What happens when the potential is not quite symmetric or when one well lies slightly above the other? Can the upper bounds (5.13) be proved to be asymptotically optimal, especially for excited states? It is likely that the methods of this paper cast some light on these questions. The question about what happens as $n \to \infty$ may be more difficult.

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