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The Twisting Trick for Double Well Hamiltonians

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Abstract. We show that the use of a twisting trick allows a transparent geometrical analysis of the spectral properties of double well Hamiltonians. In particular one can prove *norm* resolvent convergence of the relevant Hamiltonians whenever one has two centres of force whose separation R diverges to infinity.

1. Introduction

Our goal in this paper is to rederive results of Aventini and Seiler [1], Combes and Seiler [2], Morgan and Simon [8], Harrell [5, 6], Harrell and Klaus [7], and many others concerning the spectral properties of double well Hamiltonians, by a method which we hope will be easy to understand. Although our method applies to the whole range of problems above, we spell out all the details only for one simple case, and make some remarks about further developments in Sect. 4.

We consider the Hamiltonian

$$H_R = -\Delta + A(x-Re) + B(x+Re)$$

on $L^2(\mathbb{R}^3)$ as $R \to \infty$, where $e=(0,0,1)$ and A, B are potentials satisfying

(i) $A(H_0+i)^{-1}$ and $B(H_0+i)^{-1}$ are compact for $H_0 = -\Delta$,

(ii) $\|A\chi_{|x| \geqq R}\| + \|B\chi_{|x| \geqq R}\| \leqq cR^{-1}$ for large enough $R>0$.

The second condition can certainly be weakened, but the form given already suffices for many problems in quantum chemistry.

It follows from (i) that the essential spectrum of H_R (like that of H_0) equals $[0,\infty)$, so that its discrete spectrum consists of isolated negative eigenvalues of finite multiplicity with 0 as the only possible limit point. Our proposal is that one should study the discrete spectrum not of H_R but of the self-adjoint operator

$$K_R = U_R \begin{bmatrix} H_R & 0 \\ 0 & H_0 \end{bmatrix} U_R^* \tag{1}$$

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defined on

$$\mathscr{H} = L^2(\mathbb{R}^3) \oplus L^2(\mathbb{R}^3).$$

Here U_R is a unitary operator on $\mathscr{H}$, so that K_R has the same discrete spectrum with the same multiplicities as H_R. We shall show that by choosing the U_R in much the same way as in the section on the "twisting trick" in [4], (see also [10, p. 241]) it is possible to arrange that K_R converges to

$$K_\infty = \begin{bmatrix} H_0 + A & 0 \\ 0 & H_0 + B \end{bmatrix}$$

in the *norm* resolvent sense. This enables one to apply standard results concerning the spectral behaviour of K_R as $R \to \infty$, and to view the whole problem of double wells as one of *regular perturbation theory.*

2. The Main Results

We define $\theta : \mathbb{R} \to [0, \frac{\pi}{2}]$ by

$$\theta(s) = \begin{cases} \frac{\pi}{2} & \text{if} \quad s \leqq -\frac{1}{3} \\ \dfrac{\pi}{4} - \dfrac{3\pi s}{4} & \text{if} \quad -\frac{1}{3} \leqq s \leqq \frac{1}{3} \\ 0 & \text{if} \quad s \geqq \frac{1}{3}, \end{cases}$$

and the unitary operator V_R on $\mathscr{H}$ by

$$V_R(x) = \begin{bmatrix} \cos\theta(x_3/R) & \sin\theta(x_3/R) \\ -\sin\theta(x_3/R) & \cos\theta(x_3/R) \end{bmatrix},$$

so that

$$V_R(x) = \begin{cases} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \text{if} \quad x_3 \geqq R/3 \\ \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} & \text{if} \quad x_3 \leqq -R/3. \end{cases}$$

If we write

$$C_R(x) = \cos\theta(x_3/R),$$

$$S_R(x) = \sin\theta(x_3/R),$$

$$A_R(x) = A(x - Re),$$

$$B_R(x) = B(x + Re),$$

$$D_i = \frac{\partial}{\partial x_i},$$

then

$$V_R\begin{bmatrix}H_R & 0\\ 0 & H_0\end{bmatrix}V_R^*=\begin{bmatrix}H_0 & 0\\ 0 & H_0\end{bmatrix}-D_3V_R[D_3,V_R^*]-[V_R,D_3]V_R^*D_3+[D_3,V_R][D_3,V_R^*]$$
$$+\begin{bmatrix}(A_R+B_R)C_R^2 & -(A_R+B_R)C_RS_R\\ -(A_R+B_R)C_RS_R & (A_R+B_R)S_R^2\end{bmatrix}$$
$$=\begin{bmatrix}H_0+A_R & 0\\ 0 & H_0+B_R\end{bmatrix}+D_3F_R-F_RD_3+Q_R+G_R, \tag{2}$$

where F_R and Q_R are bounded matrix-valued potentials which satisfy

$$\|F_R\|=O(R^{-1}), \qquad \|Q_R\|=O(R^{-2}) \tag{3}$$

and have support in the set

$$\mathscr{C}_R=\{x:-R/3\leqq x_3\leqq R/3\}.$$

Also $G_R=G_R^*$ is the matrix-valued potential

$$G_R=\begin{bmatrix}B_RC_R^2-A_RS_R^2 & -(A_R+B_R)C_RS_R\\ -(A_R+B_R)C_RS_R & A_RS_R^2-B_RC_R^2\end{bmatrix}$$

which satisfies

$$\|G_R\|=O(R^{-1}) \tag{4}$$

as $R\to\infty$ by Hypothesis (ii).

Some geometrical insight into our various unitary transformations may be obtained from Diagram 1.

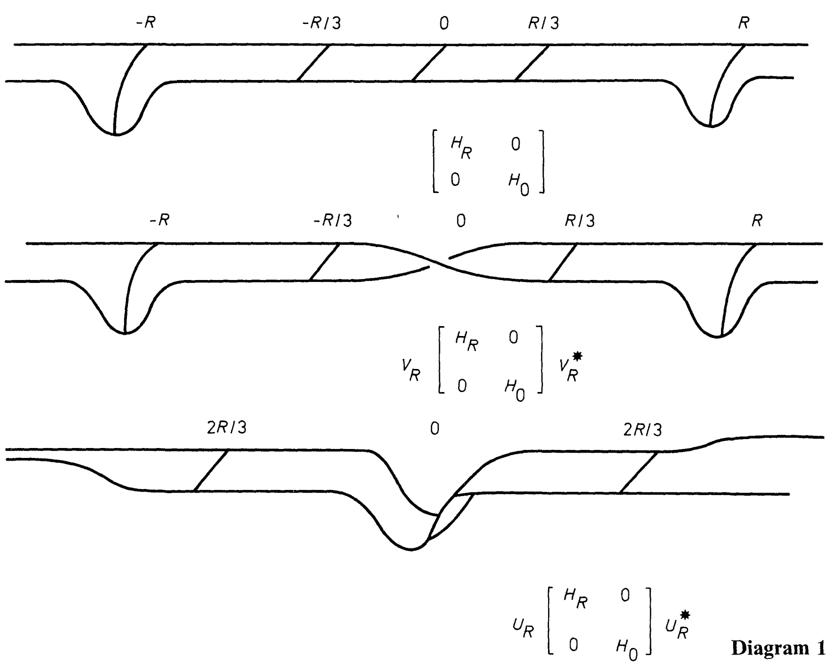

Diagram 1

We now put $U_R = W_R V_R$, where

$$W_R = \begin{bmatrix} T_R & 0 \\ 0 & T_R^* \end{bmatrix}$$

and

$$(T_R\phi)(x) = \phi(x + Re)$$

for all $\phi \in L^2(\mathbb{R}^3)$.

Theorem 1. *There is a representation*

$$K_R = K_\infty + D_3 F'_R - F'_R D_3 + Q'_R + G'_R,$$

where F'_R, Q'_R, G'_R are bounded potentials whose norms have magnitudes $O(R^{-1})$ as $R \to \infty$.

Proof. Since D_i all commute with W_R, we see that (1) and (2) immediately yield

$$K_R = \begin{bmatrix} H_0 + A & 0 \\ 0 & H_0 + B \end{bmatrix} + D_3 W_R F_R W_R^* - W_R F_R W_R^* D_3 + W_R Q_R W_R^* + W_R G_R W_R^*$$

from which the theorem follows using (3) and (4).

Corollary 2. *The operator K_R converges in the norm resolvent sense to K_∞ as $R \to \infty$.*

Proof. From the formula

$$(K_\infty + i)^{-1} - (K_R + i)^{-1} = (K_\infty + i)^{-1}(D_3 F'_R - F'_R D_3 + Q'_R + G'_R)(K_R + i)^{-1}$$

and the uniform boundedness of

$$(K_\infty + i)^{-1} D_3, \qquad D_3(K_R + i)^{-1}$$

as $R \to \infty$, we deduce that

$$\|(K_\infty + i)^{-1} - (K_R + i)^{-1}\| = O(R^{-1}).$$

It is well-known [3, p. 114; p. 289] that norm resolvent convergence implies continuity of the spectrum as $R \to \infty$, including multiplicities. Thus Corollary 2 allows us to recover Theorem 1.1 of [8] (at least for $N = 1$).

3. Asymptotics of the Eigenvalues

In order to examine *how* the eigenvalues of K_R converge to those of K_∞ we modify Theorem 1 slightly.

Theorem 3. *There is a representation*

$$K_R = K_\infty + L_R + D_3 F'_R - F'_R D_3 + Q'_R + E'_R, \tag{5}$$

where

$$L_R(x) = \begin{bmatrix} B(x + 2Re)\cos^2\theta\left(\dfrac{x + Re}{R}\right) & 0 \\ 0 & A(x - 2RE)\sin^2\theta\left(\dfrac{x - Re}{R}\right) \end{bmatrix}$$

is a potential of norm

$$\|L_R\| = O(R^{-1})$$

as $R \to \infty$. *Moreover* F'_R, Q'_R, E'_R *are bounded potentials with norms of order* R^{-1} *which all vanish on the subspace*

$$\mathscr{H}_R = \left\{ \begin{pmatrix} \phi \\ \psi \end{pmatrix} \in \mathscr{H} : \operatorname{Supp} \phi \subseteq \mathscr{C}_R, \operatorname{Supp} \psi \subseteq \mathscr{C}_R \right\}.$$

Proof. We rewrite (2) in the form

$$V_R \begin{bmatrix} H_R & 0 \\ 0 & H_0 \end{bmatrix} V_R^* = \begin{bmatrix} H_0 + A_R & 0 \\ 0 & H_0 + B_R \end{bmatrix} + \begin{bmatrix} B_R C_R^2 & 0 \\ 0 & A_R S_R^2 \end{bmatrix}$$

$$+ D_3 F_R - F_R D_3 + Q_R + E_R,$$

where the matrix-valued potential

$$E_R = -\begin{bmatrix} A_R S_R^2 & (A_R + B_R) C_R S_R \\ (A_R + B_R) C_R S_R & B_R C_R^2 \end{bmatrix}$$

satisfies

$$\|E_R\| = O(R^{-1})$$

as $R \to \infty$. The formula (5) now follows as before on observing that

$$L_R = W_R \begin{bmatrix} B_R C_R^2 & 0 \\ 0 & A_R S_R^2 \end{bmatrix} W_R^*,$$

and the last statement of the theorem may be read off the definitions of the individual terms.

The following theorem follows closely the method of [7, Theorem 3.5] and thus avoids the detailed symmetry considerations invoked in [8] to deal with the possibility of asymptotic degeneracy.

Theorem 4. *Let* E_∞ *be an n-fold degenerate negative eigenvalue of* K_∞. *Let* $E_1(R), \ldots, E_n(R)$ *and* $E'_1(R), \ldots, E'_n(R)$ *be the associated eigenvalues of* K_R *and*

$$K'_R = K_\infty + L_R$$

respectively, both series written in increasing order, so that

$$\lim_{R \to \infty} E_i(R) = \lim_{R \to \infty} E'_i(R) = E_\infty$$

for all i. Then there exists $\alpha > 0$ *such that*

$$E_i(R) - E'_i(R) = O(e^{-\alpha R})$$

as $R \to \infty$.

Proof. If P_∞ is the spectral projection of K_∞ corresponding to the eigenvalue E_∞, then it follows from the norm resolvent convergence of K_R and K'_R to K_∞ that for any small enough $\beta > 0$, the spectral projections P_R and P'_R of K_R and K'_R

respectively, for the interval $(E_\infty - \beta, E_\infty + \beta)$, have rank n for large enough R and converge in norm to P_∞.

We now compare K_R and K'_R in two stages. We see from (5) that

$$K_R = K''_R + (P'_R M_R + M_R P'_R - P'_R M_R P'_R),$$

where

$$K''_R = K'_R + (1 - P'_R) M_R (1 - P'_R)$$

and

$$M_R = D_3 F'_R - F'_R D_3 + Q'_R + E'_R.$$

The eigenvalues and eigenvectors of K''_R for the interval $(E_\infty - \beta, E_\infty + \beta)$ are exactly the same as those of K'_R provided $\beta > 0$ is small enough and $R > 0$ is large enough, because the relative bound of $(1 - P'_R) M_R (1 - P'_R)$ converges to zero. The perturbation of this part of the spectrum due to the term $(P'_R M_R + M_R P'_R - P'_R M_R P'_R)$ is exponentially small as $R \to \infty$ because (i) the eigenvectors of K'_R decrease exponentially at infinity, uniformly as $R \to \infty$, for reasons spelled out in [8], (ii) the operator M_R vanishes on the subspace $\mathscr{H}_R$, (iii) the relative bound of M_R with respect to K'_R or K''_R converges to zero as $R \to \infty$.

The point of Theorem 5 is that if we neglect exponentially small errors, then the difficult task of computing the eigenvalues $E_i(R)$ of H_R may be replaced by the much easier task of computing the eigenvalues $E'_R(R)$ of the pair of single well Hamiltonians

$$-\Delta + A(x) + B(x + 2Re) \cos^2 \theta \left(\frac{x + Re}{R} \right), \tag{6}$$

$$-\Delta + B(x) + A(x - 2Re) \sin^2 \theta \left(\frac{x - Re}{R} \right). \tag{7}$$

It turns out [8] that the eigenvalues have asymptotic expansions in R^{-1}, obtained by first replacing $A(x - 2Re)$ and $B(x + 2Re)$ by their multipole expansions.

If the double well is symmetric, that is

$$A(x) = B(-x),$$

then the Hamiltonians (6) and (7) are unitarily equivalent and so have the same eigenvalues. Therefore the eigenvalues of H_R occur in pairs with exponentially small splittings as $R \to \infty$.

4. Some Further Developments

In this section we describe two further applications of the ideas presented above. The first is to the double well anharmonic oscillator [5, 6]; double well Dirac Hamiltonians [7] could be treated similarly. Writing the basic Hamiltonian on $L^2(\mathbb{R})$ in the form

$$H_\alpha = -\frac{d^2}{dx^2} + \alpha^{-2}(x - \alpha)^2 (x + \alpha)^2 = P^2 + X_\alpha$$

one is concerned with the asymptotic degeneracy of the spectrum as $\alpha\to\infty$. One writes down an equation analogous to (1), but with

$$H_0=-\frac{d^2}{dx^2}+\alpha^2=P^2+X_\alpha(0)$$

so that the spectra of H_α and

$$\begin{bmatrix} H_\alpha & 0 \\ 0 & H_0 \end{bmatrix}$$

coincide in the interval $[0,\alpha^2)$. One then defines V_α as in Sect. 2 and gets the approximate identity

$$V_\alpha\begin{bmatrix} H_\alpha & 0 \\ 0 & H_0 \end{bmatrix}V_\alpha^*\sim\begin{bmatrix} P^2+X_R & 0 \\ 0 & P^2+X_L \end{bmatrix}$$

analogous to (2), where

$$X_R(x)=\begin{cases} X_\alpha(x) & \text{if} \quad x\geqq 0 \\ X_\alpha(0) & \text{if} \quad x<0\,, \end{cases}$$

$$X_L(x)=\begin{cases} X_\alpha(x) & \text{if} \quad x\leqq 0 \\ X_\alpha(0) & \text{if} \quad x>0\,. \end{cases}$$

Repeating our previous steps and using the symmetry of X_α about the origin, we rediscover the exponential decay of the eigenvalue gaps of H_α as $\alpha\to\infty$. We do not however obtain the exact asymptotic expressions for the gaps of [5–7].

We secondly describe the application of our method of a system composed of N electrons and two nuclei of charges Z_A and Z_B centred at Re and $-Re$ respectively, where $e=(0,0,1)$. We take the Hamiltonian on $L^2(\mathbb{R}^{3N})$ to be

$$H_R=-\sum_{r=1}^{N}(\Delta_r+Z_A|x_r-Re|^{-1}+Z_B|x_r+Re|^{-1})+W\,,$$

where

$$W(x)=\sum_{1\leqq r<s\leqq N}|x_r-x_s|^{-1}\,.$$

The idea which led to the work in this paper was the observation in [8] that it is better to study the spectral behaviour of H_R as $R\to\infty$ not in $L^2(\mathbb{R}^{3N})$ but in

$$\mathcal{M}=\bigotimes_{r=1}^{N}\{L^2(\mathbb{R}^3)\oplus L^2(\mathbb{R}^3)\}\,.$$

One may also write

$$\mathcal{M}=\sum_{a\in A}L^2(\mathbb{R}^{3N})\,,$$

where A is the set of all 2^N functions

$$a:\{1,\ldots,N\}\to\{-1,1\}\,.$$

We define the Hamiltonian $\mathscr{H}_R$ on $\mathscr{M}$ by

$$(\mathscr{H}_R f)_a = \begin{cases} H_R f_a & \text{if} \quad a = a_1 \\ H_0 f_a & \text{otherwise}, \end{cases}$$

where $a_1(i) = 1$ for all i, and

$$H_0 = -\sum_{r=1}^{N} \Delta_r + W.$$

One sees that the negative spectrum of $\mathscr{H}_R$ is unitarily equivalent to that of H_R. Defining V_R as in Sect. 2 we then derive the approximate identity

$$(\otimes^N V_R)\mathscr{H}_R(\otimes^N V_R^*) \sim \mathscr{L}_R, \tag{6}$$

where

$$(\mathscr{L}_R f)_a = L_a f_a$$

for each $a \in A$, and

$$L_a = -\sum_{r=1}^{N} \left(\Delta_r + \frac{1+a_r}{2} \frac{Z_A}{|x_r - Re|} + \frac{1-a_r}{2} \frac{Z_B}{|x_r + Re|} \right) + W.$$

That is L_a is the Hamiltonian for the N electrons when the interelectron repulsion is preserved but each electron is attracted to only one of the two nuclei, depending on the values of a.

From this point onwards one deals with each Hamiltonian L_a separately much as in the above sections. One difference is that because the electrons in each L_a are divided into two groups, but the repulsion between the two groups is still present in W (unlike the situation in [8]), one can only expect *strong* resolvent convergence after shifting the two nuclei to the origin. However the fact that the interaction energy between the two groups of electrons is positive ensures that no technical problems associated with the possible appearance of unexpected new bound states can occur.

We finally remark that because the twist in (6) is applied to all electrons equally, there is no problem in incorporating the Pauli principle into our treatment.

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