

Research Statement - Mark S. Herman

I am interested in mathematical problems in quantum mechanics arising from molecular interactions. I have studied the mathematics involved in various methods to approximate the energy and wave function corresponding to a given molecular system. Mathematically these quantities arise as the eigenvalue $E \in \mathbb{R}$ and eigenfunction $\Psi \in L^2$ of the time-independent Schrödinger equation, $H\Psi = E\Psi$. Here H is a self-adjoint operator called the Hamiltonian.

Let H_{TOT} be the Hamiltonian of a molecule of N electrons with positions x_i and mass m , moving in a field of M nuclei with positions R_k , masses M_k , and charges $Z_k > 0$. Then

$$\begin{aligned}
 H_{TOT} &= - \sum_{k=1}^M \frac{1}{2M_k} \Delta_{R_k} + h_{el}(R_1, \dots, R_M), \quad \text{where} \\
 h_{el}(R_1, \dots, R_M) &= \frac{-1}{2m} \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{|x_i - R_k|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|x_i - x_j|} \\
 &\quad + \sum_{k=1}^M \sum_{j>k}^M \frac{Z_j Z_k}{|R_j - R_k|}.
 \end{aligned}$$

The wave function satisfying $H_{TOT}\Psi_{TOT} = E_{TOT}\Psi_{TOT}$ depends on the R_k and x_i ,

$$\Psi_{TOT} =: \Psi_{TOT}(R_1, R_2, \dots, R_M, x_1, x_2, \dots, x_N) \in L^2(\mathbb{R}^{3(M+N)}).$$

The typical approach to solve the eigenvalue problem is to use the Born-Oppenheimer approximation: the large mass nuclei move very slowly compared to the small mass electrons and as a result we assume the nuclei remain at fixed positions when analyzing the motion of the electrons. We use the decomposition

$$\Psi_{TOT} = \Psi_{nuc}(R_1, \dots, R_M) \Psi_{el}(R_1, R_2, \dots, R_M; x_1, x_2, \dots, x_N), \quad (1)$$

and assuming $h_{el}(\vec{R})$, $\Psi_{el}(\vec{R})$, and $E_{el}(\vec{R})$ have only parametric dependence on $\vec{R} = (R_1, \dots, R_M)$, we seek solutions to the electronic problem

$$h_{el}(\vec{R}) \Psi_{el}(\vec{R}) = E_{el}(\vec{R}) \Psi_{el}(\vec{R}) \quad (2)$$

at all configurations \vec{R} of the nuclei. Once we obtain a solution to (2) in terms of \vec{R} , we use this to obtain Ψ_{TOT} and E_{TOT} .

I have studied two different problems related to the above decomposition. One is involved with obtaining a solution to the electronic problem and the other assumes a solution to the electronic problem, but is an interesting case where the Born-Oppenheimer approximation breaks down:

1. Divergence issues in the Møller-Plesset series

Unfortunately, the electronic problem cannot be solved exactly. There are several commonly used methods to approximate E_{el} and Ψ_{el} . One such common approach to approximate the ground state electronic energy is Møller-Plesset perturbation theory (MP theory).

For MP theory to give any meaningful information, a particular power series in terms of a complex parameter λ must have a radius of convergence greater than 1. MP theory is used extensively by theoretical chemists without knowledge of whether or not the series actually converge. The reason is that this question turns out to be very difficult. To date there is no rigorous result answering this question in any molecular system!

In collaboration with George Hagedorn, I investigated the possibility of divergence in the simplest possible case, the Helium atom. We were able to show that there is no singularity in the MP series on the real axis of λ inside the unit disk. However, we could not rule out the possibility of a singularity off of the real axis upsetting the analyticity of the series. Using a simplified model we did obtain numerical results that suggest the closest singularity is on the real axis. If we could show this rigorously, we would know MP theory is convergent for the Helium atom. We have recently written an article on this topic:

Herman, M. S. and Hagedorn, G. A., Does Møller-Plesset theory converge? A look at two-electron systems. *International Journal of Quantum Chemistry*, **109**, 210-225 (2009).

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2. Born-Oppenheimer corrections near a Renner-Teller crossing

My thesis was focused on a different problem. A triatomic molecule in the linear configuration may have a symmetry induced degeneracy in E_{el} , but when the molecule is bent the degeneracy splits. In this case, there are two electronic eigenvalues $E_1(\vec{R})$ and $E_2(\vec{R})$, that come together at a glancing intersection at the linear nuclear configuration. As a result one must use more than one solution of (2) in attempting to solve for E_{TOT} and Ψ_{TOT} . In particular the decomposition in (1) breaks down. This is called the Renner-Teller effect and has been observed experimentally. I have studied the bending modes only. In a simplified model, I considered a pair of electronic levels $E_1(\vec{R})$ and $E_2(\vec{R})$ that take part in a Renner-Teller intersection, where the equilibrium position on both electronic levels is at the linear configuration of the molecule. I use a degenerate perturbation approach to approximate E_{TOT} and Ψ_{TOT} . This appears to be the first rigorous handling of the Renner-Teller effect.

Future Research

Moving forward, I intend to apply a similar approach to study the vibrational modes of a molecule exhibiting the Renner-Teller effect in a case where the equilibrium position on one or both of the electronic levels is not the linear configuration of the molecule. A rigorous analysis could prove useful in giving approximations to the energy eigenvalues of the systems that are more accurate than those obtained from current methods.

Due to the high computational cost of solving the Schrödinger equation in many-body systems, approximation methods are of utmost importance. Often only a small portion of a system is treated quantum mechanically, while the rest of the system is studied using classical mechanics. In the context of solving for the equilibrium configuration of molecules, as well as when studying the dynamics of a system, there are very few rigorous results regarding the coupling of the quantum and classical regions of the system together. I have recently become interested in this topic, and I intend to study related questions in the near future.