

MATH 728B, MORE ON CONICAL SINGULARITIES

Recall we defined $X = X(\mathbf{R}_1, \dots, \mathbf{R}_M)$ to be the set of all electronic state functions at which the Rayleigh quotient

$$\frac{\langle\langle \psi, \mathcal{H}(\mathbf{R}_1, \dots, \mathbf{R}_M)\psi \rangle\rangle}{\langle\langle \psi, \psi \rangle\rangle}$$

assumes its minimum value $E = V(\mathbf{R}_1, \dots, \mathbf{R}_M)$. X is the eigenspace of the self-adjoint operator \mathcal{H} with eigenvalue E ; this eigenspace is finite dimensional. In class we spoke briefly about the cases $M = 1, 2$, which have special symmetry; but clearly for biomolecules $M \geq 3$ and the vectors $\mathbf{R}_1, \dots, \mathbf{R}_M$ do not lie on the same line. In this case the spin operators S^2 and S_3 are the only known observables which commute with \mathcal{H} and each other.

The significance of this can be understood provided certain aspects of the quantum formalism are kept in mind. First of all, in quantum mechanics observable quantities concerning the electrons are represented by (possibly unbounded) self-adjoint linear operators on the Hilbert space

$$\mathbb{H} = \{ \psi : (\mathbb{R}^3 \times \{0, 1\})^N \rightarrow \mathbb{C} \mid \psi \text{ is measurable, square integrable, and satisfies the anti-symmetry condition (Pauli exclusion principle)} \}.$$

Associate to any closed linear subspace S of \mathbb{H} the orthogonal projection operator P_S whose range is that subspace. If P_{S_1} and P_{S_2} are two such projection operators then we write $P_{S_1} \perp P_{S_2}$ if and only if for every pair of vectors $\psi_1 \in S_1$ and $\psi_2 \in S_2$ we have $\langle\langle \psi_1, \psi_2 \rangle\rangle = 0$, i.e. $S_1 \perp S_2$. If F is such an observable then the spectral theorem of functional analysis implies that there is a projection-valued measure dF defined on the Borel subsets of \mathbb{R} satisfying:

- (1) $dF(\emptyset) = \mathbf{0}$, $dF(\mathbb{R}) = \mathbf{1}$.
- (2) If A_1 and A_2 are any two Borel subsets of \mathbb{R} such that $A_1 \cap A_2 = \emptyset$ then $dF(A_1) \perp dF(A_2)$.
- (3) If $\{A_j\}_{j=1}^{\infty}$ is a family of Borel subsets of \mathbb{R} such that $A_j \cap A_k = \emptyset$ whenever $j \neq k$ then $dF(\cup_{j=1}^{\infty} A_j) = \sum_{j=1}^{\infty} dF(A_j)$.
- (4) For every $\psi \in D(F)$ and every $\psi' \in \mathbb{H}$ we have $\langle\langle \psi', F\psi \rangle\rangle = \int_{-\infty}^{\infty} \lambda \langle\langle \psi', dF(\lambda)\psi \rangle\rangle$.

If the molecule has the electronic state ψ and a measurement is made of the observable quantity represented by F then the predicted probability distribution of the measured values is the probability measure $A \mapsto \frac{\langle\langle \psi, dF(A)\psi \rangle\rangle}{\langle\langle \psi, \psi \rangle\rangle}$, where A is a Borel subset of \mathbb{R} . Thus in general quantum mechanics can predict only that the measured values of the quantity F will be randomly distributed according to the above distribution. If in a single such measurement the outcome is the value f_0 with instrumental uncertainty δf , then the electronic state function immediately after the measurement is defined to be $dF([f_0 - \delta f, f_0 + \delta f])\psi$. This is the statement of the famous *projection postulate* in quantum measurement theory. If λ is the only eigenvalue of the operator F in the interval $[f_0 - \delta f, f_0 + \delta f]$ then $dF([f_0 - \delta f, f_0 + \delta f])\psi = dF(\{\lambda\})\psi$ will be an eigenfunction of F with eigenvalue λ .

Measurements can be used to force a molecular system into a particular quantum state. If operators F_1, F_2, \dots, F_l pairwise commute, then all of their spectral projections $dF_1(A), dF_2(A), \dots, dF_l(A)$ commute as well, and simultaneous measurements of these quantities will result in a molecular system where the electronic state (immediately after the measurement time) is simultaneously an eigenfunction of each of the operators F_1, F_2, \dots, F_l . Suppose the observed values of F_1, F_2, \dots, F_l are f_1, f_2, \dots, f_l respectively (assumed to be isolated eigenvalues), and that the intersection of the eigenspaces $\mathcal{N}(F_1 - f_1 I) \cap \mathcal{N}(F_2 - f_2 I) \cap \dots \cap \mathcal{N}(F_l - f_l I)$ is one dimensional. Then the state function after this simultaneous observation is uniquely determined up to a nonzero complex multiple. This is the standard method of preparing a molecular system with a particular electronic state function.

It seems to be true that for a generic nuclear configuration $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ the vector space X is contained entirely in an eigenspace of \mathcal{S}^2 and the intersection of X with each of the eigenspaces of \mathcal{S}_3 is one dimensional. Thus for almost every $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ every $\psi \in X$ is an eigenvector of \mathcal{S}^2 with the same eigenvalue $S(S+1)\hbar^2$ —thus S is a locally constant function of $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ —and we can identify a particular electronic ground state function (as always, uniquely up to nonzero complex multiple) by specifying a particular eigenvalue $\hbar(S - \sigma)$, $\sigma = 0, 1, \dots, 2S$, of \mathcal{S}_3 . Thus X is a $2S + 1$ dimensional space. If $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ is a nuclear configuration where it is not true that the above assertions hold for all sufficiently nearby configurations, then we say that $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ is on a *conical singularity*. The rigorous mathematical study of such singularities is quite undeveloped. It has been pursued by the mathematician George Hagedorn. See especially his monograph: *Molecular propagation through electron energy level crossings*, Memoirs of the American Mathematical Society, **111**, (1994), no. 536. A theorem in the folklore of this field is that the Born-Oppenheimer potential $V(\mathbf{R}_1, \dots, \mathbf{R}_M)$ is an analytic function of $(\mathbf{R}_1, \dots, \mathbf{R}_M)$ away from conical singularities. A proof of such a theorem (even if I knew how to give it) is beyond the scope of this course. Most physical chemists assert strongly (but without hint of mathematical justification) that conical singularities only occur at configurations whose energies are much higher than the energies of configurations occurring in normal biological contexts. For example, if $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ is on a conical singularity of the water molecule, and $(\mathbf{R}_1^0, \mathbf{R}_2^0, \mathbf{R}_3^0)$ is an equilibrium configuration of the water molecule then $V(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - V(\mathbf{R}_1^0, \mathbf{R}_2^0, \mathbf{R}_3^0)$ is about 5 electron volts, or about $8 \cdot 10^{-19}$ Joule. This means that in a solution of water at room temperature a water “molecule” in the configuration $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ is e^{-39} times as likely to occur as a water molecule in the standard equilibrium configuration $(\mathbf{R}_1^0, \mathbf{R}_2^0, \mathbf{R}_3^0)$. Thus it is an assumption in biomolecular dynamics that the Born-Oppenheimer potential is a smooth function for all the nuclear configurations of interest. It is safe to say that precisely stated and proved theorems concerning the above topics are open research problems.