Math2121420
The Coulomb potential
Rayleigh-Ritz,
Approximation methods.

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Outline

I first will prove that the $1/r$ potential is H_0 bounded with $a < 1$ with respect to the free Hamiltonian H_0, i.e. satisfies

$$\|V\phi\| \le a\|H_0\phi\| + b\|\phi\| \quad \text{with } a < 1, \tag{1}$$

when $V = 1/r$. This implies via Kato-Rellich that $H = H_0 - Z/r$ is self adjoint with domain $D(H_0)$. In fact, we can prove (1) holds with a arbitrarily small. (All this in three dimensions.)

The method will also prove that the essential spectrum of H is the same as that of H_0. So the negative spectrum of H consists of eigenvalues of finite multiplicity.

I will then describe the famous “Rayleigh-Ritz” method of approximating those eigenvalues of an operator below the essential spectrum and discuss applications to chemistry.

1. Potentials in $L_2 \oplus L_\infty$
2. Rayleigh-Ritz and its applications.
    - Variations on the variational formula.
    - The secular equation.
3. Valence.
    - Two dimensional examples.
    - The Hückel theory of hydrocarbons.

Potentials in $L_2 \oplus L_\infty$

Suppose that $V = V_1 + V_2$ with $V_1 \in L_2(\mathbb{R}^3)$ and V_2 a bounded measurable function. For example, if $V = 1/r$, take $V_1 = \mathbf{1}_{B_1} \cdot \frac{1}{r}$ and $V_2 = V - V_1$. Since $1/r$ is locally square integrable near the origin in three dimensions, and since $\sup|V - V_1| \leq 1$ we have such a decomposition.

We will show that such a V satisfies (1) with a arbitrarily small. Since V_2 is bounded, we have $\|V_2\psi\| \leq \|M\|\psi\|$ for some M, and this can be absorbed into the b in (1). So we must estimate $\|V_1\psi\|$.

Estimating $\|V_1\psi\|$

If $\psi \in D(H_0)$ we have

$$\psi(x) = \frac{1}{2\pi)^{\frac{3}{2}}} \int (c+p^2)^{-1}(c+p^2)\hat{\psi}(p)e^{ip\cdot x}dp$$

for any $c > 0$. So

$$\sup|\psi| \leq \frac{1}{(2\pi)^{\frac{3}{2}}} \left(\int (c+p^2)^{-1}dp\right)^{\frac{1}{2}} (\|H_0\psi\| + c\|\psi\|).$$

The integral can be made as small a we like by choosing c large. Now

$$\|V_1\psi\| \leq \|V_1\| \sup|\psi|$$

giving our desired estimate (1). $\square$

Add the assumption that $V(x) \to 0$ as $x \to \infty$

If the potential satisfies (1) and, in addition, satisfies $V(x) \to 0$ as $x \to \infty$ then $H_0 + V$ has the same essential spectrum as H_0, namely $[0, \infty)$.
Indeed, the resolvent if H_0 at -1 is $-\frac{1}{1+\|p\|^2}$. Now $\frac{1}{1+\|p\|^2} \cdot V_1$ is Hilbert Schmidt, and $\frac{1}{1+\|p\|^2} \cdot V_2$ is compact (as we proved in the last lecture), so Weyl guarantees that $H_0 + V$ has the same essential spectrum as H_0.

The (negative) eigenvalues of $H_0 - \frac{Z}{r}$ can be calculated explicitly, and are calculated in most quantum mechanics books. This is usually done by writing down the partial differential equation which is formally equivalent to the eigenvalue problem, and solving it by separation of variables. There are two gaps in this argument: it is not clear a priori that every eigenfunction of the Hilbert space operator is sufficiently smooth to be a (classical) solution of the differential equation.

Indeed, our treatment of the square well depended on the fact that in one dimension, elements of the domain of H_0 were continuously differentiable, which need not be true in higher dimensions.

Also, it is not clear that all solutions of the equation are obtained by separation of variables.

A correct and complete treatment can be found in the paper "Atomic Hamiltonians and the HVZ Theorem" by Kevin McLeod, available on the web. One of the key ideas is a version of the Sobolev space type argument that we used (following Hermann Weyl) to show that eigenvectors of elliptic operators are indeed smooth - in this case smooth away from the origin. I do not want to go into this, referring to McLeod's paper.

But we *do* know from Hardy's inequality that all eigenvalues are $\geq -Z^2$. There are no eigenvalues going off to $-\infty$. In the physics literature this is known as the "stability of matter" for the case of the hydrogen atom - the electron can not collapse into the nucleus. In general, the problem of the stability of matter is a major industry, including the work of such eminent mathematicians such as Lieb.

Some history.

Instead of an exact calculation, I will discuss an extremely important method of approximate calculation known generaly as the "Rayleigh-Ritz" method. I will follow the treatment in the book *Spectral theory and differential operators* by Davies. Lord Rayleigh was one of the most famous physicists of the 19th-20th century, winning the Nobel prize for his discovery of Argon, for example. What his relation to the "Rayleigh-Ritz" method? Here is the abstract of a paper "The historical bases of the Rayleigh and Ritz methods" by A.W. Leissa which appeared in the *Journal of Sound and Vibration*, Vol. 287, pp. 961-978: Rayleigh's classical book *Theory of Sound* was first published in 1877. In it are many examples of calculating fundamental natural frequencies of free vibration of continuum systems (strings, bars, beams, membranes, plates) by assuming the mode shape, and setting the maximum values of potential and kinetic energy in a cycle of motion equal to each other...

This procedure is well known as Rayleigh's Method. In 1908, Ritz laid out his famous method for determining frequencies and mode shapes, choosing multiple admissible displacement functions, and minimizing a functional involving both potential and kinetic energies. He then demonstrated it in detail in 1909 for the completely free square plate. In 1911, Rayleigh wrote a paper congratulating Ritz on his work, but stating that he himself had used Ritz's method in many places in his book and in another publication. Subsequently, hundreds of research articles and many books have appeared which use the method, some calling it the Ritz method and others the Rayleigh-Ritz method. The present article examines the method in detail, as Ritz presented it, and as Rayleigh claimed to have used it. It concludes that, although Rayleigh did solve a few problems which involved minimization of a frequency, these solutions were not by the straightforward, direct method presented by Ritz and used subsequently by others. Therefore, Rayleigh's name should not be attached to the method.

Who was Ritz?

Walther Ritz (22 February 1878 - 7 July 1909) was a Swiss theoretical physicist. His father, Raphael Ritz, a native of Valais, was a well-known landscape and interior scenes artist. His mother was the daughter of the engineer Noerdlinger of Tübingen. Ritz studied in Zurich and Göttingen. He is most famous for his work with Johannes Rydberg on the Rydberg-Ritz combination principle. Ritz is also known for the variational method named after him, the Ritz method. Ritz died in 1909, at the age of 31. According to Forman's Dictionary of Scientific Biography, Ritz contracted tuberculosis in 1900, which led to his death in 1909. According to Ritz's collected works L the disease was pleurisy.

Rayleigh-Ritz.

Let H be a non-negative self-adjoint operator on a Hilbert space $\mathfrak{H}$. For any finite dimensional subspace L of $\mathfrak{H}$ with $L \subset \mathcal{D} = \mathrm{Dom}(H)$ define

$$\lambda(L) := \sup\{(Hf, f) | f \in L \text{ and } \|f\| = 1\}.$$

Define

$$\lambda_n = \inf\{\lambda(L), \quad |L \subset \mathcal{D}, \text{ and } \dim L = n\}. \tag{2}$$

The λ_n are an increasing family of numbers. We shall show that they constitute that part of the discrete spectrum of H which lies below the essential spectrum:

Let H be a non-negative self-adjoint operator on a Hilbert space $\mathfrak{H}$. Define the numbers $\lambda_n = \lambda_n(H)$ by (2). Then one of the following three alternatives holds:

1. H has empty essential spectrum. In this case the $\lambda_n \to \infty$ and coincide with the eigenvalues of H repeated according to multiplicity and listed in increasing order, or else $\mathfrak{H}$ is finite dimensional and the λ_n coincide with the eigenvalues of H repeated according to multiplicity and listed in increasing order.
2. There exists an $a < \infty$ such that $\lambda_n < a$ for all n, and $\lim_{n\to\infty} \lambda_n = a$. In this case a is the smallest number in the essential spectrum of H and $\sigma(H) \cap [0, a)$ consists of the λ_n which are eigenvalues of H repeated according to multiplicity and listed in increasing order.
3. There exists an $a < \infty$ and an N such that $\lambda_n < a$ for $n \leq N$ and $\lambda_m = a$ for all $m > N$. Then a is the smallest number in the essential spectrum of H and $\sigma(H) \cap [0, a)$ consists of the $\lambda_1, \ldots, \lambda_N$ which are eigenvalues of H repeated according to multiplicity and listed in increasing order.

Let b be the smallest point in the essential spectrum of H (so $b = \infty$ in case 1.). So H has only isolated eigenvalues of finite multiplicity in $[0, b)$ and these constitute the entire spectrum of H in this interval. Let $\{f_k\}$ be an orthonormal set of these eigenvectors corresponding to these eigenvalues μ_k listed (with multiplicity) in increasing order.

We want to show that

$$\lambda_n = \mu_n.$$

$\lambda_n \leq \mu_n$.

Let M_n denote the space spanned by the first n of these eigenvectors, and let $f \in M_n$. Then $f = \sum_{j=1}^{n}(f, f_j)f_j$ so

$$Hf = \sum_{j=1}^{n} \mu_j (f, f_j) f_j$$

and so

$$(Hf, f) = \sum_{j=1}^{n} \mu_j |(f, f_j)|^2 \leq \mu_n \sum_{j=1}^{n} |(f, f_j)|^2 = \mu_n \|f\|^2$$

so

$$\lambda_n \leq \mu_n.$$

In the other direction, let L be an n-dimensional subspace of $\mathrm{Dom}(H)$ and let P denote orthogonal projection of $\mathfrak{H}$ onto M_{n-1} so that

$$Pf = \sum_{j=1}^{n-1}(f, f_j)f_j.$$

The image of P restricted to L has dimension at most $n-1$ while L has dimension n. So there must be some $f \in L$ with $Pf = 0$. By the multiplicative version of the spectral theorem, the function $\tilde{f} = Uf$ corresponding to f is supported in the set where $h \geq \mu_n$ and hence $(Hf, f) \geq \mu_n \|f\|^2$ so

$$\lambda_n \geq \mu_n.$$

We have proved that $\lambda_n = \mu_n$.

There are now three cases to consider: If $b = +\infty$ (i.e. the essential spectrum of H is empty) then $\lambda_n = \mu_n$ can have no finite accumulation point so we are in case 1). If there are infinitely many μ_n in $[0, b)$ they must have a finite accumulation point $a \leq b$, and by definition, a is in the essential spectrum. Then we must have $a = b$ and we are in case 2).

The remaining possibility is that there are only finitely many $\mu_1, \dots \mu_M < b$. Then for $k \leq M$ we have $\lambda_k = \mu_k$ as above, and also $\lambda_m \geq b$ for $m > M$. Since $b \in \sigma_{\mathrm{ess}}(H)$, the space

$$K := P(b-\epsilon, b+\epsilon)\mathfrak{H}$$

is infinite dimensional for all $\epsilon > 0$. Let $\{f_1, f_2, \dots,\}$ be an orthonormal basis of K, and let L be the space spanned by the first m of these basis elements. By the spectral theorem, $(Hf, f) \leq (b+\epsilon)\|f\|^2$ for any $f \in L$. So for all m we have $\lambda_m \leq b + \epsilon$. So we are in case 3). ☐

In applications (say to chemistry) one deals with self-adjoint operators which are bounded from below, rather than being non-negative. But this requires just a trivial shift in stating and applying the preceding theorem. In some of these applications the bottom of the essential spectrum is at 0, and one is interested in the lowest eigenvalue λ_1 which is negative.

The hydrogen atom.

Here is a famous application of the method: The Hamiltonian for the hydrogen atom is

$$H = \frac{\hbar^2}{2m}\Delta - \frac{e^2}{\kappa_0 r}$$

where $\kappa_0 = 4\pi\epsilon_0$ and ϵ_0 is the permittivity of free space, and m and e are the mass and charge of the electron.

We want to minimize

$$\frac{(H\psi,\psi)}{(\psi,\psi)}$$

to find the lowest eigenvalue.

Suppose we try functions of r alone, $\psi = \psi(r)$. Then

$$(\Delta\psi)(r) = -\psi''(r) - \frac{2}{r}\psi'(r).$$

More specifically, try

$$\psi(r) = e^{-cr}.$$

Then

$$(H\psi)(r) = \left[\frac{\hbar^2}{2m}\left(-c^2 + \frac{2c}{r}\right) - \frac{e^2}{\kappa_0 r}\right] e^{-cr}.$$

In doing the integrals (with respect to $r^2 \sin\theta dr d\theta d\phi$) observe that

$$\int_0^\infty e^{-2cr}dr = \frac{1}{2c}, \quad \int_0^\infty re^{-2cr}dr = \frac{1}{4c^2}, \quad \int_0^\infty r^2e^{-2cr}dr = \frac{1}{4c^3}$$

so

$$\frac{(H\psi,\psi)}{(\psi,\psi)} = \frac{\hbar^2}{2m}c^2 - \frac{e^2c}{\kappa_0}.$$

The minimum over c is achieved at

$$c = \frac{me^2}{\kappa_0\hbar^2}$$

giving the value

$$\frac{(H\psi,\psi)}{(\psi,\psi)} = -\frac{me^4}{2\kappa_0^2\hbar^2}.$$

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It turns out that this is in fact the lowest eigenvalue of H. This is due to our choice of exponential function as trial function. Had we chosen a Gaussian as trial function, we would be off by around 15%.

The Bohr radius.

According to Bohr's 1913 theory of the hydrogen atom, the electron moves around the nucleus in a circle of radius

$$a_0 := \frac{\kappa_0 \hbar^2}{me^2}.$$

We see that the value of c that we found for the minimum is $1/a_0$. So if we choose our units of length so that $a_0 = 1$ (the so called "atomic units") then $c = 1$ and

$$\lambda_1 = -\frac{e^2}{2\kappa_0}.$$

In fact, in these units the function e^{-r} is an eigenvector of H with the lowest eigenvalue λ_1.

The hydrogen molecule.

In 1929 Dirac made the outrageous statement

> *"The underlying physical laws necessary for the mathematical theory of a large part of physics and all of chemistry are thus completely known."*

I want to examine how this works, in particular how Rayleigh-Ritz enters into the "theory"' of the hydrogen molecule.

A starting approximation is to assume that the nucleus is a point particle. That is, we ignore the fact that the nucleus is composed of protons and neutrons, and that these are made of quarks etc.

The Born-Oppenheimer approximation (1927).

The next approximation is to treat the nuclei as fixed (at a distance R from one another) and try to solve the Schrödinger operator for the pair of electrons, in particular to find its lowest eigenvalue. Add to this lowest eigenvalue (the so-called "electronic energy") the energy of repulsion between the nuclei to obtain a function $E(R)$. Then search for the R which minimizes $E(R)$.

The Hamiltonian of the electrons, expressed in units of $\frac{e^2}{a_0}$, has the form

$$\frac{1}{2}\Delta_1^2 + \frac{1}{2}\Delta_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}.$$

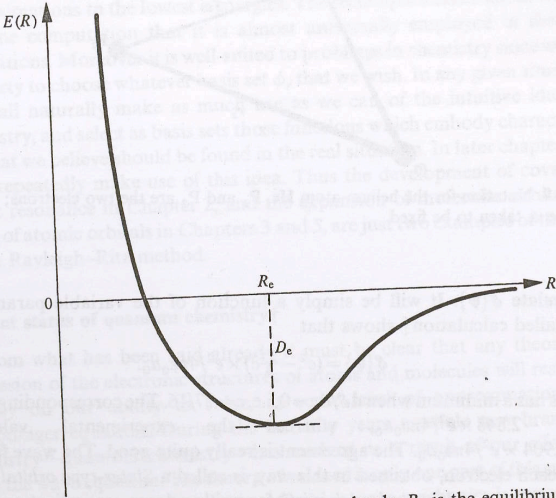

FIG. 6. Potential-energy curve for a diatomic molecule. R_e is the equilibrium bond length, D_e is the dissociation energy, no account being taken of the zero-point vibrational motion.

The Heitler-London “theory” (1927).

If the nuclei are very far apart, we expect the ground state to be given by the tensor product of the ground states of the individual hydrogen atoms, there being no interaction between them. If we call the nuclei a and b, and the corresponding ground states ϕ_a and ϕ_b then we might expect the combined ground state to be of the form $\phi_a \otimes \phi_b$. So we might expect that the combined ground state be of the form $\phi_a(1) \otimes \phi_b(2)$ where the notation $\phi_a(1)$ implies that it is electron 1 which is near nucleus a.

But how do we know that it is electron 1 and not electron 2 which is around nucleus a?

Heitler-London, continued.

So Heitler and London suggested that we apply Rayleigh-Ritz using the two dimensional subspace of the tensor product spanned by $\phi_a(1) \otimes \phi_b(2)$ and $\phi_a(2) \otimes \phi_b(1)$.

On the basis of symmetry, we can conclude that the extrema of the quadratic form restricted to this two dimensional subspace must be at the combinations

$$\Phi_\pm := \phi_a(1) \otimes \phi_b(2) \pm \phi_a(2) \otimes \phi_b(1).$$

The value of the quadratic form evaluated on Φ_+ or Φ_- is reduced to an integal. These integrals were difficult to evaluate, and it took another year for their evaluation. But then one obtained two curves, one corresponding to Φ_+ which was of the form of the figure, and one corresponding to Φ_- which had no minimum.

Heitler-London, continued.

The minimum for Φ_+ indicated an equilibrium bond length of 87 pm, compared with the observed experimental value of 74 pm, and a disassociation energy of 3.14 ev compared with the experimental value 4.75 ev. Not bad!

In 1916 the chemist G.N. Lewis proposed a "theory" of the "covalent bond" as being due to the "sharing of two electrons" between the two atoms. The Heitler-London use of Rayleigh-Ritz might be considered as a derivation of the Lewis theory.

This is the "valence bond" theory of Hetler, London, Pauling and Slater. Other"theories" are currently in use.

Heitler, Linus and Ava Pauling, London.

An alternative formulation of the R.-R. formula.

Instead of (2) we can determine the λ_n as follows: We define λ_1 as before:

$$\lambda_1 = \min_{f \neq 0} \frac{(Hf, f)}{(f, f)}.$$

Suppose that f_1 is an f which attains this minimum. We then know that f_1 is an eigenvector of H with eigenvalue λ_1. Now define

$$\lambda_2 := \min_{f \neq 0, f \perp f_1} \frac{(Hf, f)}{(f, f)}.$$

This λ_2 coincides with the λ_2 given by (2) and an f_2 which achieves the minimum is an eigenvector of H with eigenvalue λ_2.

Proceeding this way, after finding the first n eigenvalues $\lambda_1, \dots, \lambda_n$ and corresponding eigenvectors $f_1, \dots, f_n$ we define

$$\lambda_{n+1} = \min_{f \neq 0, f \perp f_1, f \perp f_2, \dots, f \perp f_n} \frac{(Hf, f)}{(f, f)}.$$

This gives the same λ_k as (2).

Variations on the condition $L \subset \mathrm{Dom}(H)$.

In some applications, the condition $L \subset \mathrm{Dom}(H)$ is unduly restrictive, especially when we want to compare eigenvalues of different self adjoint operators. In these applications, one can frequently find a common **core** $\mathcal{D}$ for the quadratic forms Q associated to the operators. That is,

$$\mathcal{D} \subset \mathrm{Dom}(H^{\frac{1}{2}})$$

and $\mathcal{D}$ is dense in $\mathrm{Dom}(H^{\frac{1}{2}})$ for the metric $\|\cdot\|_1$ given by

$$\|\|f\|_1^2 = Q(f,f) + \|f\|^2$$

where

$$Q(f,f) = (Hf,f).$$

Theorem

Define

$$\begin{aligned}
\lambda_n &= \inf\{\lambda(L), \ |L \subset \mathrm{Dom}(H) \quad \dim L = n \\
\lambda'_n &= \inf\{\lambda(L), \ |L \subset \mathcal{D} \quad \dim L = n \\
\lambda''_n &= \inf\{\lambda(L), \ |L \subset \mathrm{Dom}(H^{\frac{1}{2}}) \quad \dim L = n.
\end{aligned}$$

Then

$$\lambda_n = \lambda'_n = \lambda''_n.$$

Proof that $\lambda'_n = \lambda''_n$.

Since $\mathcal{D} \subset \mathrm{Dom}(H^{\frac{1}{2}})$ the condition $L \subset \mathcal{D}$ implies $L \subset \mathrm{Dom}(H^{\frac{1}{2}})$ so

$$\lambda'_n \geq \lambda''_n \quad \forall\ n.$$

Conversely, given $\epsilon > 0$ let $L \subset \mathrm{Dom}(H^{\frac{1}{2}})$ be such that L is n-dimensional and

$$\lambda(L) \leq \lambda''_n + \epsilon.$$

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Restricting Q to $L \times L$, we can find an orthonormal basis $f_1, \ldots, f_n$ of L such that

$$Q(f_i, f_j) = \gamma_i \delta_{ij}, \quad 0 \leq \gamma_1 \leq \cdots, \gamma_n = \lambda(L).$$

We can then find $g_i \in \mathcal{D}$ such that $\|g_i - f_i\|_1 < \epsilon$ for all $i = 1, \ldots, n$. This means that

$$|a_{ij} - \delta_{ij}| < c_n \epsilon, \quad \text{where} \quad a_{ij} := (g_i, g_j)$$

and

$$|b_{ij} - \gamma_i \delta_{ij}| < c'_n \epsilon \quad \text{where} \quad b_{ij} := Q(g_i, g_j),$$

and the constants c_n and c'_n depend only on n.

Let L' be the space spanned by the g_i. Then L' is an n-dimensional subspace of $\mathcal{D}$ and

$$\lambda(L') = \sup\{\sum_{ij=1}^{n} b_{ij} z_i \overline{z}_j | \quad \sum_{ij}^{n} a_{ij} z_i \overline{z}_j \leq 1\}$$

satisfies

$$|\lambda(L') - \lambda''_n| < c''_n \epsilon$$

where c''_n depends only on n. Letting $\epsilon \to 0$ shows that $\lambda'_n \leq \lambda''_n$.

To complete the proof of the theorem, it suffices to show that $\mathrm{Dom}(H)$ is a core for $\mathrm{Dom}(H^{\frac{1}{2}})$. This follows from the spectral theorem: The domain of H is unitarily equivalent to the space of all f such that

$$\int_S (1 + h(s,n)^2)|f(s,n)|^2 d\mu < \infty$$

where $h(s,n) = s$. This is clearly dense in the space of f for which

$$\|f\|_1 = \int_S (1 + h)|f|^2 d\mu < \infty$$

since h is non-negative and finite almost everywhere.

The secular equation.

The definition (2) makes sense in a real finite dimensional vector space: If Q is a real quadratic form on a finite dimensional real Hilbert space V, then we can write $Q(f) = (Hf, f)$ where H is a self-adjoint (=symmetric) operator, and then find an orthonormal basis according to (2). In terms of such a basis $f_1, \dots, f_n$, we have

$$Q(f) = \sum_k \lambda_k r_k^2 \quad \text{where} \quad f = \sum r_k f_k.$$

If we consider the problem of finding an extreme point of $Q(f)$ subject to the constraint that $(f,f)=1$, this becomes (by Lagrange multipliers), the problem of finding λ and f such that

$$dQ_f = \lambda dS_f, \text{where}\ \ S(f) = (f,f).$$

In terms of the coordinates $(r_1,\dots,r_n)$ we have

$$\frac{1}{2}dQ_f = (\mu_1 r_1,\dots,\mu_n r_n)\ \ \text{while}\quad \frac{1}{2}dS_f = (r_1,\dots,r_n).$$

So the only possible values of λ are $\lambda=\mu_i$ for some i and the corresponding f is given by $r_j=0,\ j\neq i$ and $r_i\neq 0.$ This is a watered down version version of Rayleigh-Ritz.

In applications, one is frequently given a basis of V which is *not* orthonormal. Thus (in terms of the given basis)

$$Q(f) = \sum H_{ij} r_i r_j, \quad \text{and} \quad S(f) = \sum_{ij} S_{ij} r_i r_j$$

where

$$f = \sum r_i f_i.$$

The problem of finding an extreme point of $Q(f)$ subject to the constraint $S(f) = 1$ becomes that of finding λ and $r = (r_1, \dots, r_n)$ such that

$$dQ_f = \lambda dS_f.$$

The problem of finding an extreme point of $Q(f)$ subject to the constraint $S(f) = 1$ becomes that of finding λ and $r = (r_1, \ldots, r_n)$ such that

$$dQ_f = \lambda dS_f$$

i.e. i.e.

$$\begin{pmatrix} H_{11} - \lambda S_{11} & H_{12} - \lambda S_{12} & \cdots & H_{1n} - \lambda S_{1n} \\ \vdots & \vdots & \vdots & \vdots \\ H_{n1} - \lambda S_{n1} & H_{n2} - \lambda S_{n2} & \cdots & H_{nn} - \lambda S_{nn} \end{pmatrix} \begin{pmatrix} r_1 \\ \vdots \\ r_n \end{pmatrix} = 0.$$

As a condition on λ this becomes the algebraic equation

$$\det \begin{pmatrix} H_{11} - \lambda S_{11} & H_{12} - \lambda S_{12} & \cdots & H_{1n} - \lambda S_{1n} \\ \vdots & \vdots & \vdots & \vdots \\ H_{n1} - \lambda S_{n1} & H_{n2} - \lambda S_{n2} & \cdots & H_{nn} - \lambda S_{nn} \end{pmatrix} = 0$$

which is known as the secular equation due to its previous use in astronomy to determine the periods of orbits.

Back to chemistry.

The minimum eigenvalue λ_1 is determined according to (2) by

$$\lambda_1 = \inf_{\psi \neq 0} \frac{(H\psi, \psi)}{(\psi, \psi)}.$$

Unless one has a clever way of computing λ_1 by some other means, minimizing the expression on the right over all of $\mathfrak{H}$ is a hopeless task. What is done in practice is to choose a finite dimensional subspace and apply the above minimization over all ψ in that subspace (and similarly to apply (2) to subspaces of that subspace for the higher eigenvalues). The hope is that this yield good approximations to the true eigenvalues. We saw how this worked in the Heitler London theory.

If M is a finite dimensional subspace of $\mathfrak{H}$, and P denotes projection onto M, then applying (2) to subspaces of M amounts to finding the eigenvalues of PHP, which is an algebraic problem as we have seen. A **chemical theory** (when H is the Schrödinger operator) then amounts to cleverly choosing such a subspace.

Consider the case where M is two dimensional with a basis ψ_1 and ψ_2. The idea is that we have some grounds for believing that that the true eigenfunction has characteristics typical of these two elements and is likely to be some linear combination of them. If we set

$$H_{11} := (H\psi_1, \psi_1), \quad H_{12} := (H\psi_1, \psi_2) = \overline{H_{21}}, \quad H_{22} := (H\psi_2, \psi_2)$$

and

$$S_{11} := (S\psi_1, \psi_1), \quad S_{12} := (\psi_1, \psi_2) = \overline{S_{21}}, \quad S_{22} := (\psi_2, \psi_2)$$

then if these quantities are real we can apply the secular equation

$$\det \begin{pmatrix} H_{11} - \lambda S_{11} & H_{12} - \lambda S_{12} \\ H_{21} - \lambda S_{21} & H_{22} - \lambda S_{22} \end{pmatrix} = 0$$

to determine λ.

Suppose that $S_{11} = S_{22} = 1$, i.e. that ψ_1 and ψ_2 are separately normalized. Also assume that ψ_1 and ψ_2 are linearly independent. Let

$$\beta := S_{12} = S_{21}.$$

This β is sometimes called the "overlap integral" since if our Hilbert space is $L_2(\mathbb{R}^3)$ then $\beta = \int_{\mathbb{R}^3} \psi_1 \overline{\psi}_2 dx$. Now

$$H_{11} = (H\psi_1, \psi_1)$$

is the guess that we would make for the lowest eigenvalue (= the lowest "energy level") if we took L to be the one dimensional space spanned by ψ_1. So let us call this value E_1. So $E_1 := H_{11}$ and similarly define $E_2 = H_{22}$. The secular equation becomes

$$(\lambda - E_1)(\lambda - E_2) - (H_{12} - \lambda\beta)^2 = 0.$$

$$(\lambda - E_1)(\lambda - E_2) - (H_{12} - \lambda\beta)^2 = 0.$$

If we define $F(\lambda) := (\lambda - E_1)(\lambda - E_2) - (H_{12} - \lambda\beta)^2$ then F is positive for large values of $|\lambda|$ since $|\beta| < 1$ by Cauchy-Schwarz. $F(\lambda)$ is non-positive at $\lambda = E_1$ or E_2 and in fact generically will be strictly negative at these points. So the lower solution of the secular equations will generically lie strictly below $\min(E_1, E_2)$ and the upper solution will generically lie strictly above $\max(E_1, E_2)$. This is known as the **no crossing rule** and is of great importance in chemistry.

The Hückel theory of hydrocarbons.

In this theory the space M is the n-dimensional space where each carbon atom contributes one electron. (The other electrons being occupied with the hydrogen atoms.) It is assumed that the S in the secular equation is the identity matrix. This amounts to the assumption that the basis given by the electrons associated with each carbon atom is an orthonormal basis. It is also assumed that $(Hf, f) = \alpha$ is the same for each basis element. In a crude sense this measures the electron-attracting power of each carbon atom and hence is assumed to be the same for all basis elements.

If $(Hf_r, f_s) \neq 0$, the atoms r and s are said to be "bonded". It is assumed that only "nearest neighbor" atoms are bonded, in which case it is assumed that $(Hf_r, f_s) = \beta$ is independent of r and s. So PHP has the form

$$\alpha I + \beta A$$

where A is the adjacency matrix of the graph whose vertices correspond to the carbon atoms and whose edges correspond to the bonded pairs of atoms. If we set

$$x := \frac{E - \alpha}{\beta}$$

then finding the energy levels is the same as finding the eigenvalues x of the adjacency matrix A. In particular this is so if we assume that the values of α and β are independent of the particular molecule.