Hartree-Fock Excited States

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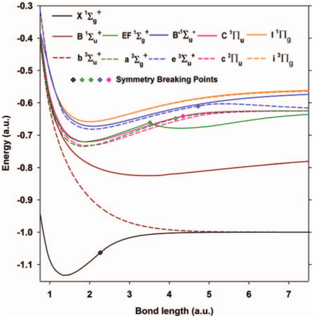
Conference on "Mathematical challenges in classical & quantum statistical mechanics"
Venice, August 2017

HF Excited States

- **Hartree-Fock theory:**
  - simplest nonlinear approx. of fermionic N-particle ground state problem
  - not always efficient (correlation) $\rightsquigarrow$ Kohn-Sham / DFT
  - recently discovery: can be efficient for excited states



THE JOURNAL OF CHEMICAL PHYSICS **141**, 111104 (2014)

Communication: Hartree-Fock description of excited states of H_2

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(Received 8 August 2014; accepted 10 September 2014; published online 19 September 2014)

Hartree-Fock (HF) theory is most often applied to study the electronic ground states of molecular systems. However, with the advent of numerical techniques for locating higher solutions of the self-consistent field equations, it is now possible to examine the extent to which such mean-field solutions are useful approximations to electronic excited states. In this Communication, we use the maximum overlap method to locate 11 low-energy solutions of the HF equation for the H_2 molecule and we find that, with only one exception, these yield surprisingly accurate models for the low-lying excited states of this molecule. This finding suggests that the HF solutions could be useful first-order approximations for correlated excited state wavefunctions.

N-particle Schrödinger operator

N-particle fermionic Hamiltonian

$$H^V(N) = \sum_{j=1}^{N} -\Delta_{x_j} + V(x_j) + \sum_{1\leq j<k\leq N} w(x_j - x_k)$$

V, w infinitesimally relatively $-\Delta$–form bounded in $\mathbb{R}^d$

Ground state energy

$$E^V(N) = \min \mathrm{Spec}_{\bigwedge_1^N L^2(\mathbb{R}^d)}\left(H^V(N)\right) = \inf_{\substack{\Psi\in\bigwedge_1^N H^1(\mathbb{R}^d)\\ \|\Psi\|=1}} \left\langle \Psi, H^V(N)\Psi\right\rangle$$

Bottom of essential spectrum

$$\Sigma^V(N) = \min \mathrm{Ess\ Spec}_{\bigwedge_1^N L^2(\mathbb{R}^d)}\left(H^V(N)\right) = \inf_{\substack{\Psi_n\rightharpoonup 0\\ \|\Psi_n\|=1}} \liminf_{n\to\infty} \left\langle \Psi_n, H^V(N)\Psi_n\right\rangle$$

HVZ Theorem

Excited state energies

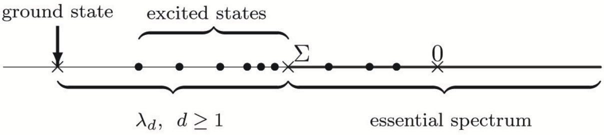
$$\lambda_k^V(N) = \inf_{\substack{\mathcal{V}\subset\bigwedge_1^N H^1(\mathbb{R}^d)\\ \dim(\mathcal{V})=k}} \max_{\substack{\Psi\in\mathcal{V}\\ \|\Psi\|=1}} \langle\Psi, H^V(N)\Psi\rangle$$

is the kth eigenvalue of $H^V(N)$, counted with multiplicity, or $= \Sigma^V(N)$.

Theorem (HVZ)

$$\Sigma^V(N) = \min\left\{E^V(N-k) + E^0(k),\ \ k = 1, ..., N\right\}$$

(Hunziker '66, Van Winter '64, Zhislin '60)

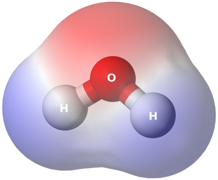


Atoms & Molecules

- **Atoms & Molecules** (Born-Oppenheimer):

$$V(x) = -\sum_{m=1}^{M} \frac{z_m}{|x - R_m|}, \qquad w(x) = \frac{1}{|x|}$$

Since $w \geq 0$, $E^0(k) = 0$, hence $\Sigma^V(N) = E^V(N-1)$



$M = 3,\ N = 10$
$z_1 = z_2 = 1,\ z_3 = 8$

Theorem (Spectrum of atoms & molecules)

- *If* $N < \sum_{m=1}^{M} z_m + 1$ *then* $\lambda_k^V(N) < \Sigma^V(N)$ *for all* $k \geq 1$.

(Zhislin '60, Zhislin-Sigalov '65)

- *If* $N \geq \sum_{m=1}^{M} z_m + 1$ *then* $\lambda_{k_0}^V(N) = \Sigma^V(N)$ *for some* $k_0 \geq 1$.

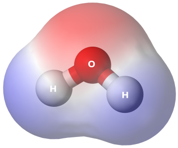
(Yafaev '76, Vugalter-Zhislin '77, Sigal '82)

- *If* $N \gg 1$ *(e.g.* $N \geq 2\sum_{m=1}^{M} z_m + 1$*), then* $k_0 = 1$.

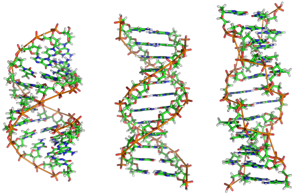
(Lieb '84, Nam '12, Ruskai '82, Sigal '82-84, Lieb-Sigal-Simon-Thirring '88, Seco-Sigal-Solovej '90, Fefferman-Seco '90, Lenzmann-Lewin '13)

Curse of dimensionality

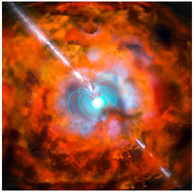
$$\left\{\sum_{j=1}^{N} -\Delta_{x_j} + V(t,x_j) + \sum_{1\leq j<k\leq N} w(x_j - x_k)\right\}\Psi(t,x_1,\ldots,x_N) = \begin{cases} i\dfrac{\partial}{\partial t}\Psi(t,x_1,\ldots,x_N) \\ \lambda\,\Psi(x_1,\ldots,x_N)\end{cases}$$



$N = 10$ electrons in water molecule



$N \sim 10^3$ in small macromolecules (short segments of DNA)



$N \sim 10^{57}$ in neutron star

"the mathematical theory of a large part of physics and the whole of chemistry is thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed"

Dirac (1929)

Hartree-Fock theory

Hartree-Fock state

$$\Psi = \varphi_1 \wedge \cdots \wedge \varphi_N = \frac{1}{\sqrt{N!}} \det(\varphi_j(x_k))$$

where $\varphi_j \in L^2(\mathbb{R}^d, \mathbb{R})$ and $\langle \varphi_j, \varphi_k \rangle = \delta_{jk}$

- Restrict N-particle energy to manifold $\mathcal{M} = \{\Psi = \varphi_1 \wedge \cdots \wedge \varphi_N\}$

$$\left\langle \Psi, H^V(N)\Psi \right\rangle = \sum_{j=1}^N \int_{\mathbb{R}^3} |\nabla\varphi_j|^2 + V|\varphi_j|^2$$

$$+ \frac{1}{2} \iint_{\mathbb{R}^6} w(x-y) \left(\sum_{j=1}^N |\varphi_j(x)|^2 \sum_{k=1}^N |\varphi_k(y)|^2 - \left| \sum_{j=1}^N \varphi_j(x)\varphi_j(y) \right|^2 \right) dx\, dy$$

$$= \sum_{j=1}^N \int_{\mathbb{R}^3} |\nabla\varphi_j|^2 + V|\varphi_j|^2 + \sum_{1 \le j < k \le N} \iint_{\mathbb{R}^6} w(x-y)\, |\varphi_j \wedge \varphi_k(x,y)|^2\, dx\, dy$$

$$h_\Psi \varphi_j = \mu_j \varphi_j, \qquad j = 1, ..., N$$

$$h_\Psi f := \left(-\Delta + V + \textstyle\sum_{j=1}^N |\varphi_j|^2 * w \right) f - \textstyle\sum_{j=1}^N \left((\varphi_j f) * w \right) \varphi_j$$

Hartree-Fock ground states

Hartree-Fock ground state energy

$$E^V_{\rm HF}(N) = \inf_{\substack{\Psi\in\mathcal{M}\\ \|\Psi\|=1}} \left\langle \Psi, H^V(N)\Psi\right\rangle \geq E^V(N)$$

Theorem (Existence of HF ground states)

Let V, w be infinitesimally $-\Delta$–form bounded in $\mathbb{R}^d$. The following are equivalent:

(i) *All the minimizing sequences $\{\Psi_n\}\subset\mathcal{M}$ for $E^V_{\rm HF}(N)$ have a convergent subsequence in $H^1(\mathbb{R}^{dN})$*

(ii) $E^V_{\rm HF}(N) < E^V_{\rm HF}(N-k) + E^0_{\rm HF}(k)$ *for all* $k = 1,...N$

(Friesecke '03, Lewin '11)

Rmk. Sort of **nonlinear HVZ**. Very important that HF = restriction of $H^V(N)$

Atoms and molecules: existence for $N < \sum_{m=1}^{M} z_m + 1$ (Lieb-Simon '77, Lions '87)

Weyl $\equiv$ Palais-Smale condition

Exercise

Linear problem with $E^V(N) < \Sigma^V(N)$.

1. Any minimizing sequence $\{\Psi_n\}$ for $E^V(N)$ is precompact
2. $\exists$ non-compact sequences $\{\Psi_n\}$ such that $\langle\Psi_n, H^V(N)\Psi_n\rangle \to c < \Sigma^V(N)$
3. If $(H^V(N) - c)\Psi_n \to 0$ (Weyl) with $c < \Sigma^V(N)$, then $\{\Psi_n\}$ is precompact

Proof of 3)

- Extract subsequence such that $\Psi_n \rightharpoonup \Psi$
- Passing to weak limits gives $(H^V(N) - c)\Psi = 0$

$$c \leftarrow \langle\Psi_n, H^V(N)\Psi_n\rangle = \underbrace{\langle\Psi, H^V(N)\Psi\rangle}_{c\|\Psi\|^2} + \underbrace{\langle(\Psi_n - \Psi), H^V(N)(\Psi_n - \Psi)\rangle}_{\geq \Sigma^V(N)(1-\|\Psi\|^2)+o(1)} + o(1)$$

Weyl $\equiv$ Palais-Smale condition II

Theorem: HF Palais-Smale condition (Lewin '17)

Assume $w \geq 0$ and $E^V_{\rm HF}(N) < E^V_{\rm HF}(N-1)$. Let $\Psi_n = \varphi_{1,n} \wedge \cdots \wedge \varphi_{N,n} \in \mathcal{M}$ with

- $\langle \Psi_n, H^V(N)\Psi_n \rangle \to c \in \big[E^V_{\rm HF}(N), E^V_{\rm HF}(N-1)\big)$,
- $h_{\Psi_n}\varphi_{j,n} - \mu_{j,n}\varphi_{j,n} \to 0$ in $H^{-1}(\mathbb{R}^d)$, $\forall j = 1, ..., N$, $\quad [\partial_{\mathcal{M}}\mathcal{E}^V(\Psi_n) \to 0]$

then $\{\Psi_n\}$ is precompact in $H^1(\mathbb{R}^{dN})$ and converges strongly, after extraction of a subsequence, to $\Psi = \varphi_1 \wedge \cdots \wedge \varphi_N \in \mathcal{M}$ which is a Hartree-Fock critical point.

HF Excited states

Theorem: HF Excited States (Lewin '17)

For atoms and molecules with $N < \sum_{m=1}^M z_m + 1$, the HF energy has infinitely many critical points $\{\Psi^{(k)}\}_{k\geq 1}$ on $\mathcal{M}$ with energies

$$\lambda_k^V(N) \leq \lambda_{\mathrm{HF},k}^V(N) = \left\langle \Psi^{(k)}, H^V(N)\Psi^{(k)} \right\rangle < E_{\mathrm{HF}}^V(N-1), \qquad k \geq 1$$

such that

$$\lim_{k\to\infty} \lambda_{\mathrm{HF},k}^V(N) = E_{\mathrm{HF}}^V(N-1)$$

Rmk. Lions '87 also constructed infinitely many HF critical point, but with energies $\left\langle \Psi^{(k)}, H^V(N)\Psi^{(k)} \right\rangle \to 0$ ($\simeq$ "embedded eigenvalues")

- Lions worked in one-particle space, his method applies to other HF-like theories
- I work in N-particle space, the method uses that HF = restriction linear problem on $\mathcal{M}$

Critical Point Theory

Nonlinear minimax method

$$\lambda^V_{\mathrm{HF},k}(N) := \inf_{\substack{f:\,\mathbb{S}^{k-1}\to\mathcal{M}\\ \text{continuous and odd}}} \sup_{\Psi\in f(\mathbb{S}^{k-1})} \left\langle \Psi, H^V(N)\Psi \right\rangle \leq E^V_{\mathrm{HF}}(N-1)$$

- generalizes usual Courant-Fischer / Rayleigh-Ritz linear minimax
- $\lambda^V_k(N)$ =same formula on whole sphere instead of $\mathcal{M}$
- one can use instead Krasnoselskii index, homology classes, etc
- Palais-Smale at minimax level $\Longrightarrow \exists$ critical point
- Palais-Smale does **not** hold for energies< 0, Lions uses Morse index bounds to get compactness

(Ambrosetti-Rabinowitz '73, Berestycki-Lions '83, Rabinowitz '86,...)

Proof of Palais-Smale property

Lemma (Geometric limits of HF states)

If $\mathcal{M} \ni \Psi_n \rightharpoonup \Psi$, then

$$\liminf_{n\to\infty} \mathcal{E}^V(\Psi_n) \geq \left(1 - \|\Psi\|^2\right) \min_{k=1,\dots,N} \left\{ E^V_{\rm HF}(N-k) + E^0_{\rm HF}(k) \right\} + \mathcal{E}^V(\Psi).$$

(Friesecke '03, Lewin '11)

Main fact: the (geometric) localization of a pure HF state is a convex combination of HF pure states

Lemma (Energy of weak limit of Palais-Smale sequence)

Assume $w \geq 0$. If $\mathcal{M} \ni \Psi_n \rightharpoonup \Psi$ with $\mathcal{E}^V(\Psi_n) \to c$ and $\partial_{\mathcal{M}}\mathcal{E}^V(\Psi_n) \to 0$, then

$$\mathcal{E}^V(\Psi) \geq c\|\Psi\|^2$$