Seeking “identity” for real-space open quantum subsystems

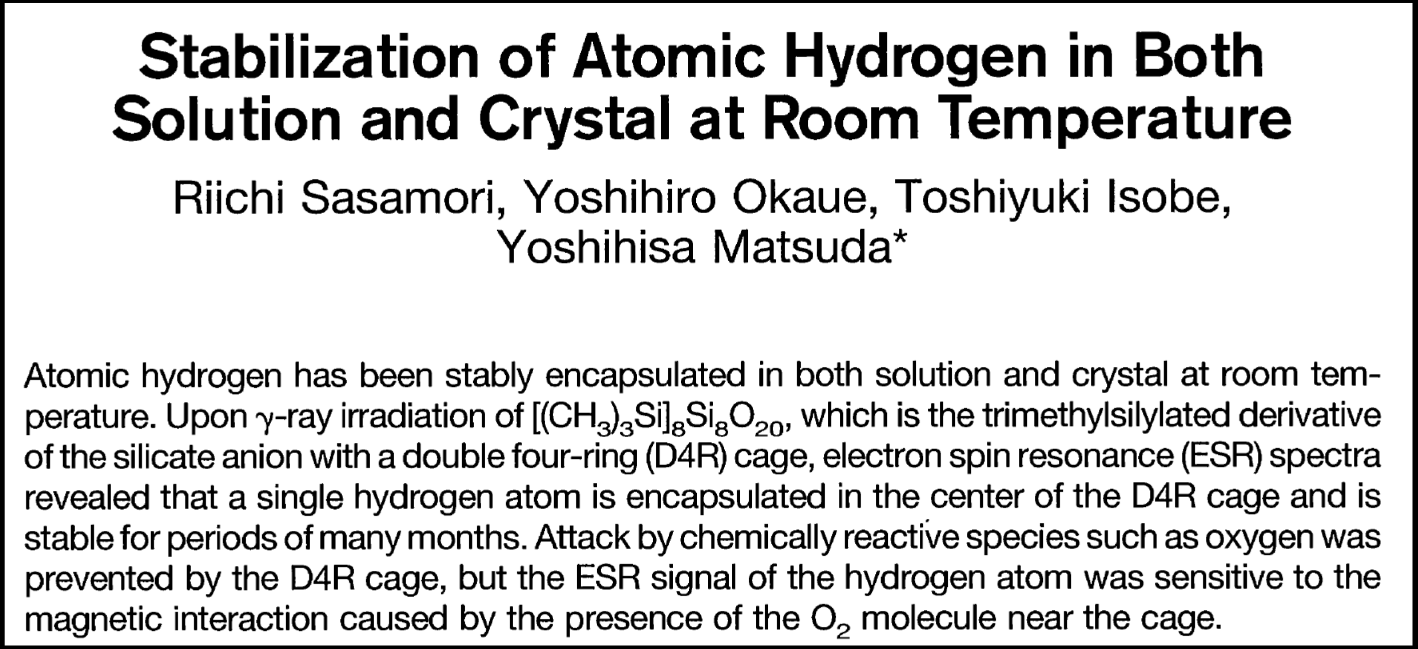
Shant Shahbazian

Faculty of Physics

Shahid Beheshti University

Prepared by Shant Shahbazian for the conference "The imporatnt role of the fundational physics in the future evolution of science" held at the Institute for research in fundamental sciences (IPM) (19-Dec-2017)

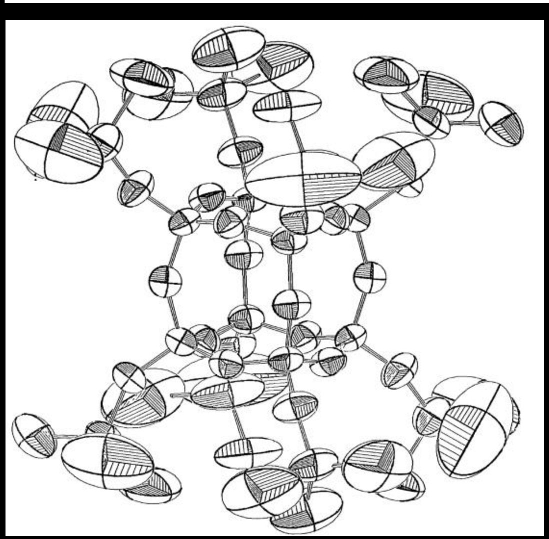
Science 265, 1691 (1994)

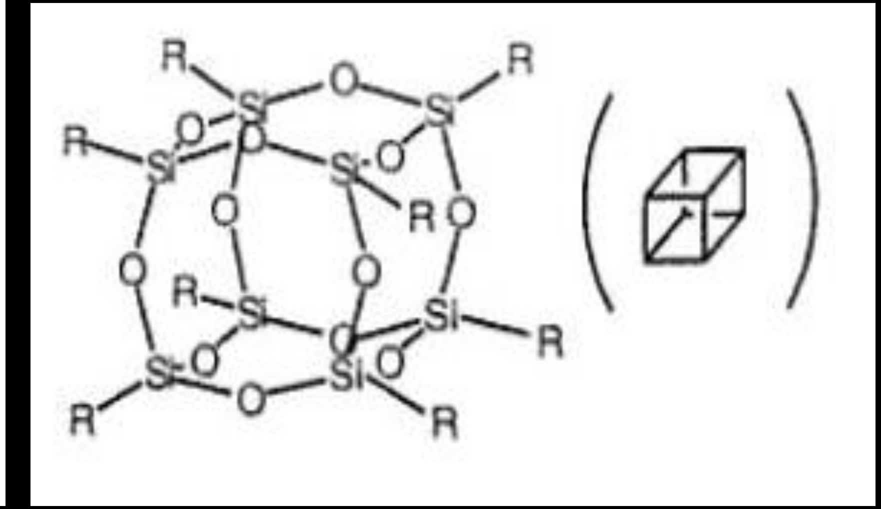


Stabilization of Atomic Hydrogen in Both Solution and Crystal at Room Temperature

Riichi Sasamori, Yoshihiro Okaue, Toshiyuki Isobe, Yoshihisa Matsuda*

Atomic hydrogen has been stably encapsulated in both solution and crystal at room temperature. Upon γ-ray irradiation of $[(CH_3)_3Si]_8Si_8O_{20}$, which is the trimethylsilylated derivative of the silicate anion with a double four-ring (D4R) cage, electron spin resonance (ESR) spectra revealed that a single hydrogen atom is encapsulated in the center of the D4R cage and is stable for periods of many months. Attack by chemically reactive species such as oxygen was prevented by the D4R cage, but the ESR signal of the hydrogen atom was sensitive to the magnetic interaction caused by the presence of the O_2 molecule near the cage.





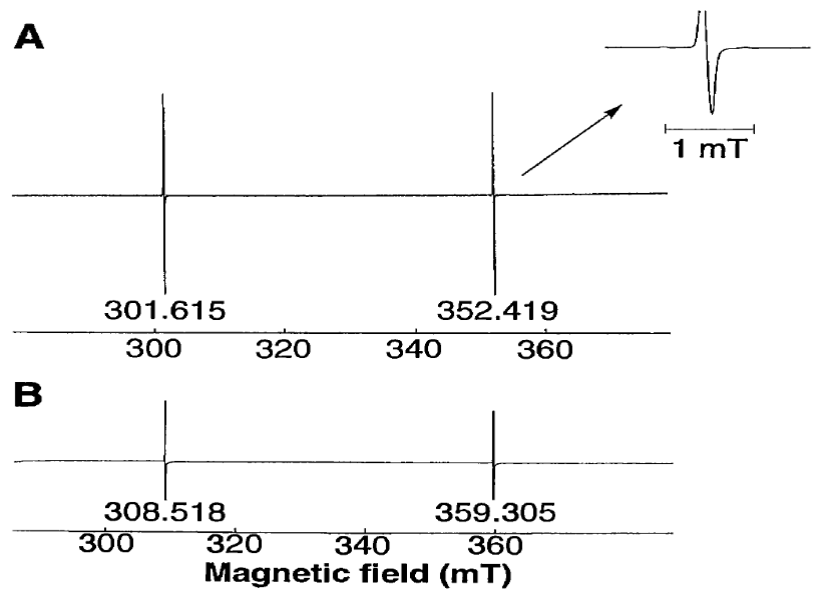
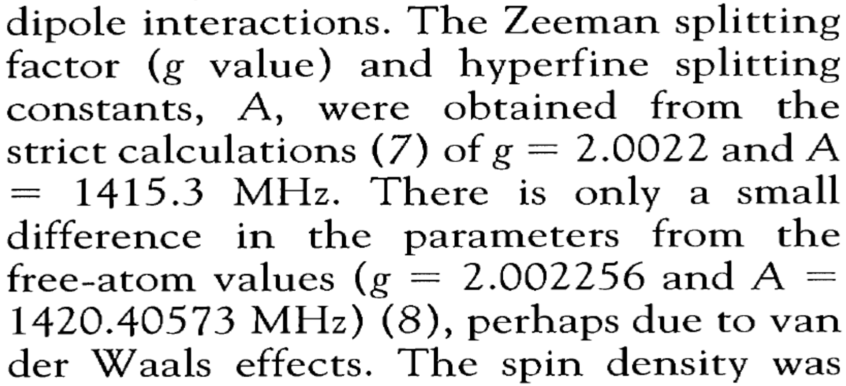
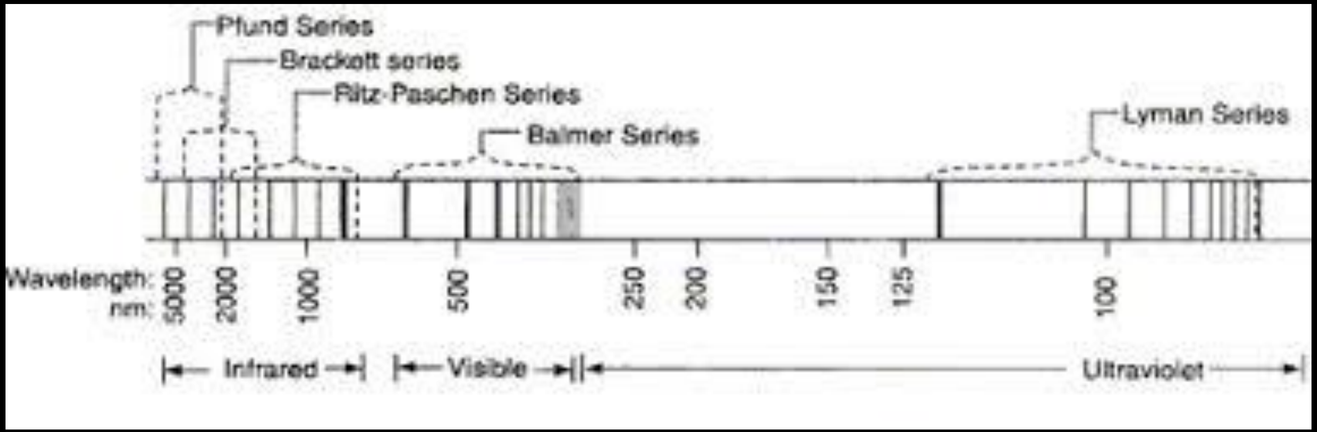
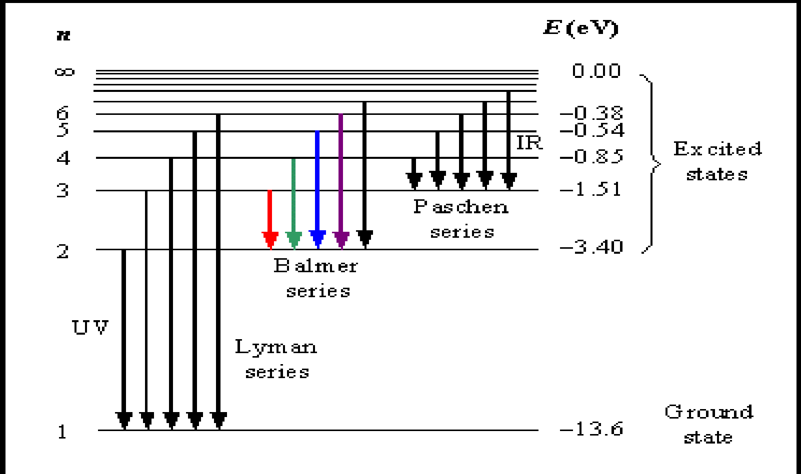


Fig. 2. (**A**) ESR spectrum of atomic hydrogen in γ-irradiated polycrystalline $[(CH_3)_3Si]_8Si_8O_{20}$ at room temperature (microwave frequency, ν, of 9.2185 GHz). (**B**) ESR spectrum for diethyl ether solution of γ-irradiated specimen (ν = 9.4128 GHz).



dipole interactions. The Zeeman splitting factor (g value) and hyperfine splitting constants, A, were obtained from the strict calculations (7) of $g = 2.0022$ and $A = 1415.3$ MHz. There is only a small difference in the parameters from the free-atom values ($g = 2.002256$ and $A = 1420.40573$ MHz) (8), perhaps due to van der Waals effects. The spin density was





Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated

$$\hat{H}_H = \left(-\hbar^2/2\mu\right)\nabla^2 - \left(1/\left|\vec{r}_e - \vec{r}_p\right|\right), \quad \hat{H}_H\Psi_H = E_H\Psi_H$$

Trapped hydrogen atom in cavity ⇒

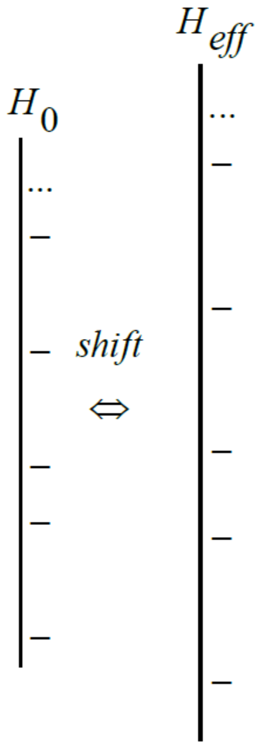
⇒ shift in energy levels

$$\hat{H}_{trapped-H} = \hat{H}_H + \overbrace{\hat{V}_{environment}}^{?}$$

$$\hat{V}_{environment} = \begin{cases} (1/2)K_e\left(\vec{r}_e - \vec{r}_0\right)^2 + (1/2)K_p\left(\vec{r}_p - \vec{r}_0\right)^2 \\ \sum_i^N \left\{-\left(\alpha/\left|\vec{r}_{CM} - \vec{r}_i\right|^6\right) + \left(\beta Exp\left[-\gamma\left|\vec{r}_{CM} - \vec{r}_i\right|\right]/\left|\vec{r}_{CM} - \vec{r}_i\right|\right)\right\} \\ \dots \end{cases}$$

General strategy $\Rightarrow \hat{H}_{effective} = \hat{H}_{system} + \hat{V}_{environment}(\alpha, \beta, \gamma, \ldots)$

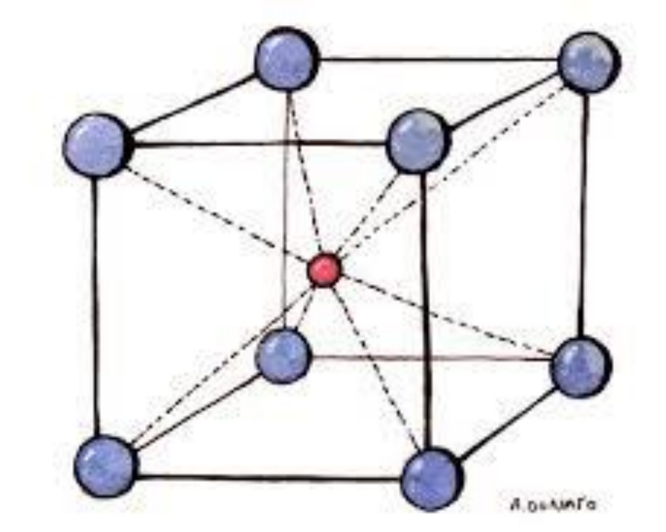
$$\hat{H}_{effective} = \overbrace{\underbrace{\overbrace{\hat{H}_{system}}^{\hat{H}_0} + \overbrace{\hat{V}_{environment}}^{\hat{H}'}}_{\text{variational}}}^{\text{perturbation theory}} \Rightarrow \text{energy spectrum}$$



$\Rightarrow$ comparision to experiment

$system \Rightarrow quantum\ identity$

$environment \Rightarrow ghost\ identity$



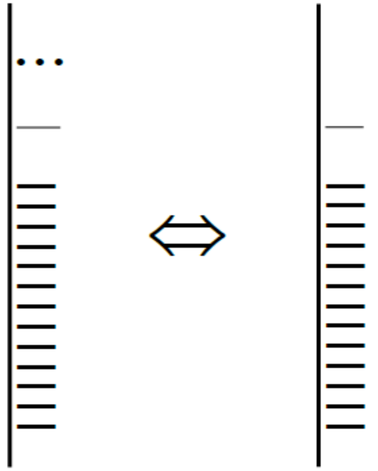
Let's consider part of the environment explicitly Since environment is composed of atoms and since atoms are composed of electrons and nuclei the Hamiltonian of the large system is:

$$\Rightarrow \hat{H}^{\text{large}}_{system} = \hat{T}_{elec} + \hat{T}_{nuc} + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}$$

$$\hat{H}^{\text{large}}_{system} \overset{?}{\Rightarrow} \hat{H}^{\text{small}}_{system}$$

$$\hat{H}^{\text{large}}_{effective} = \hat{H}^{\text{large}}_{system} + \hat{V}^{small}_{environment} \Rightarrow$$

$H^{\text{large}}_{effective}$ $\Leftrightarrow$ $H^{small}_{effective}$



$$\text{large } system \Rightarrow quantum\ identity$$

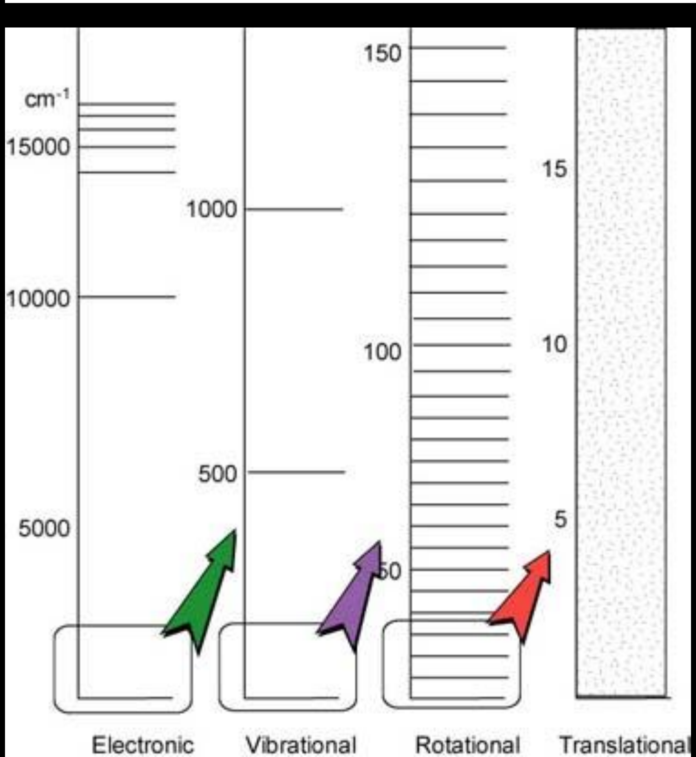
$$environment \Rightarrow ghost\ identity$$

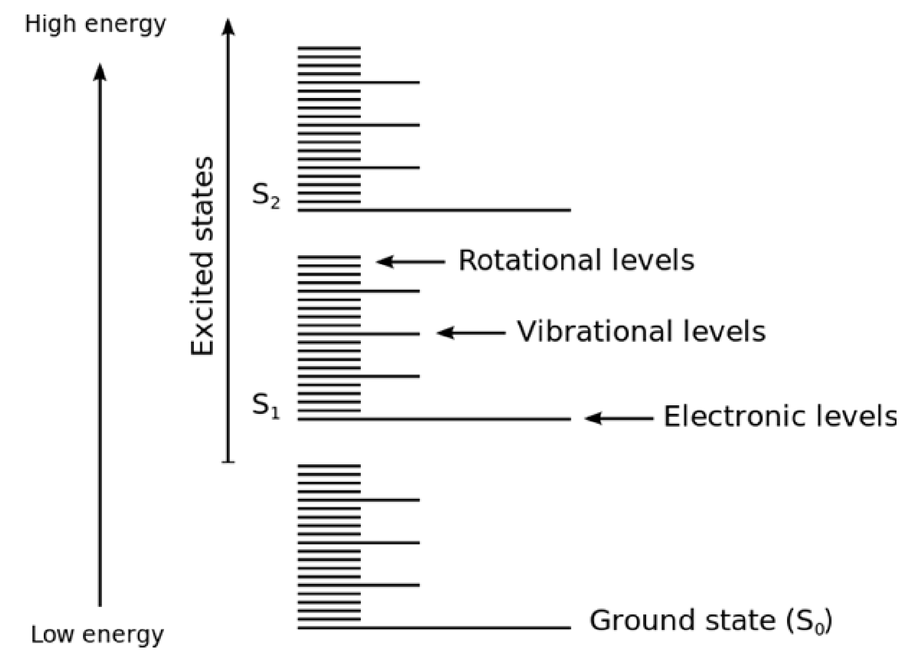
$$small\ system \Rightarrow subsystem \Rightarrow ?$$

Are there examples of quantum subsystems?

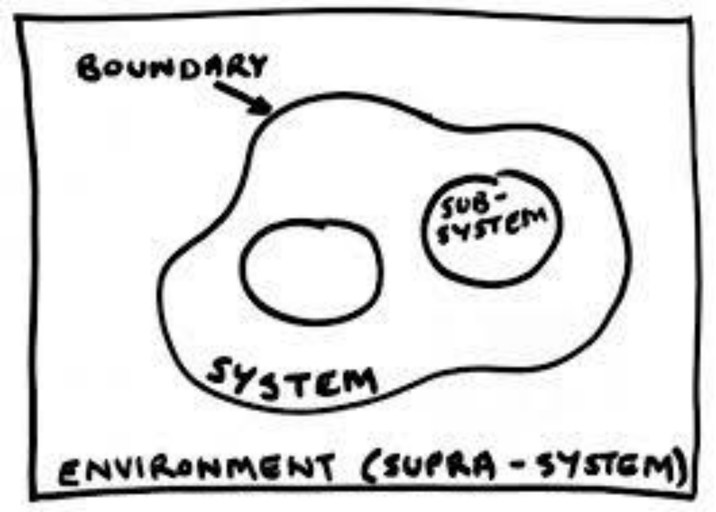
The idea of decoupled degrees of freedom may serve as an example (Born-Oppenheimer approximation, etc.)

$$\hat{H}_{system} = \overbrace{\sum_{i}^{k} \hat{H}^{i}_{subsystem}}^{\hat{H}_0} + \overbrace{\sum_{i>j}^{k} \alpha_{ij} \hat{H}^{i,j}_{couplings}}^{\hat{H}'} \overset{\{\alpha\}\text{ are small}}{\approx} \sum_{i}^{k} \hat{H}^{i}_{subsystem} \Rightarrow \Psi_{system} \approx \prod_{i}^{k} \psi^{i}_{subsystem}$$

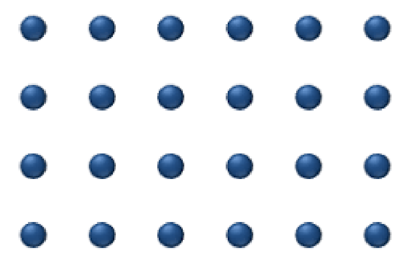




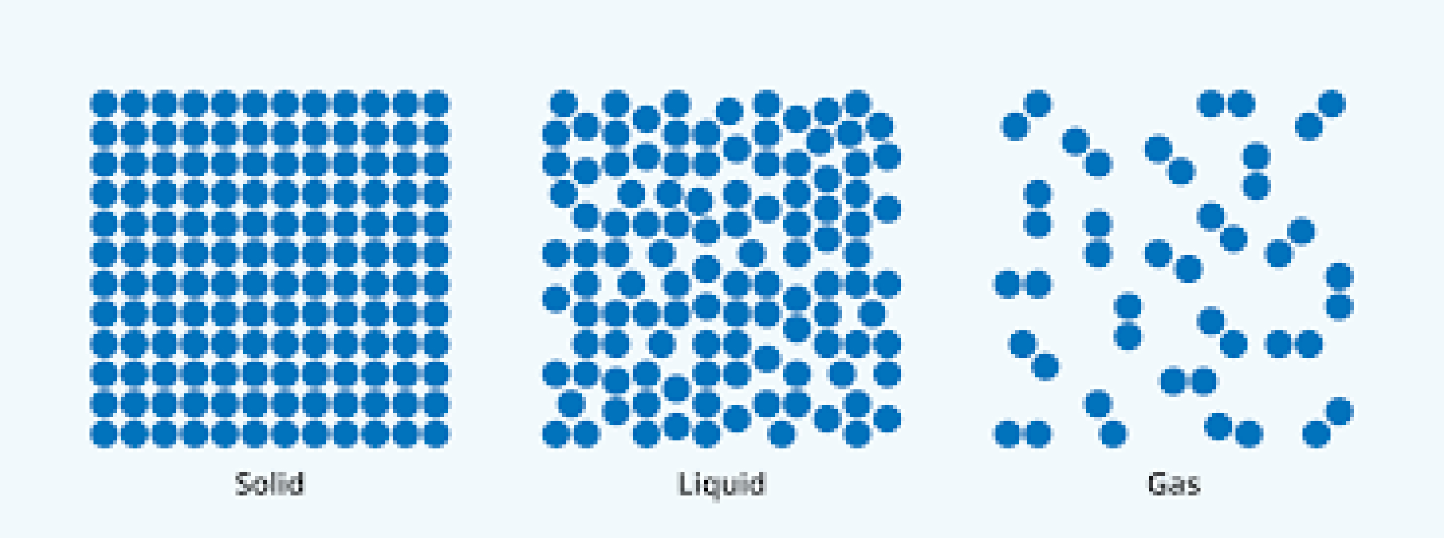
Take home lessen: As far as part of the energy spectrum of the system is reproducible by an effective Hamiltonian, this part of spectrum corresponds to a subsystem, having its own Hilbert space and "semi-autonomous" **identity**

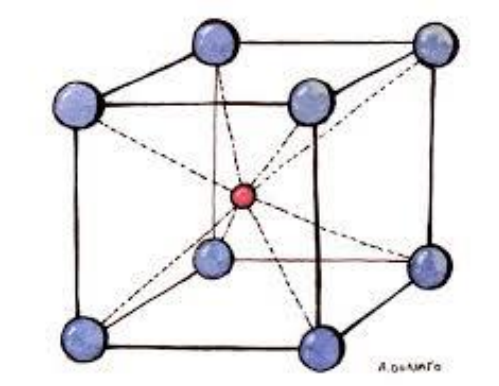


Note that all this scheme is in Hilbert space!



$$\text{Generalization} \Rightarrow \hat{H}_{system} = \overbrace{\sum_{i}^{M} \hat{H}^{i}_{free-atom}}^{\hat{H}^{(0)}} + \overbrace{\sum_{i>j}^{M} V_{\text{int}}(i,j)}^{\hat{H}'}$$

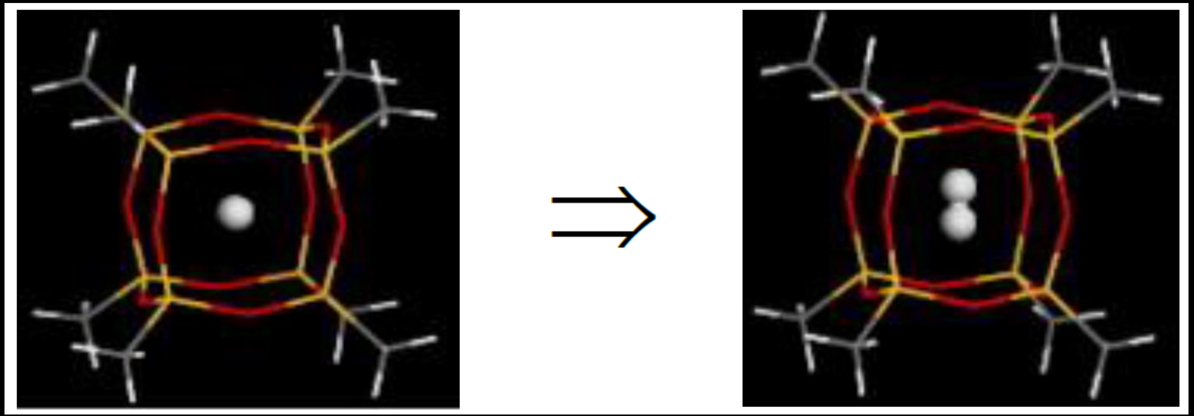


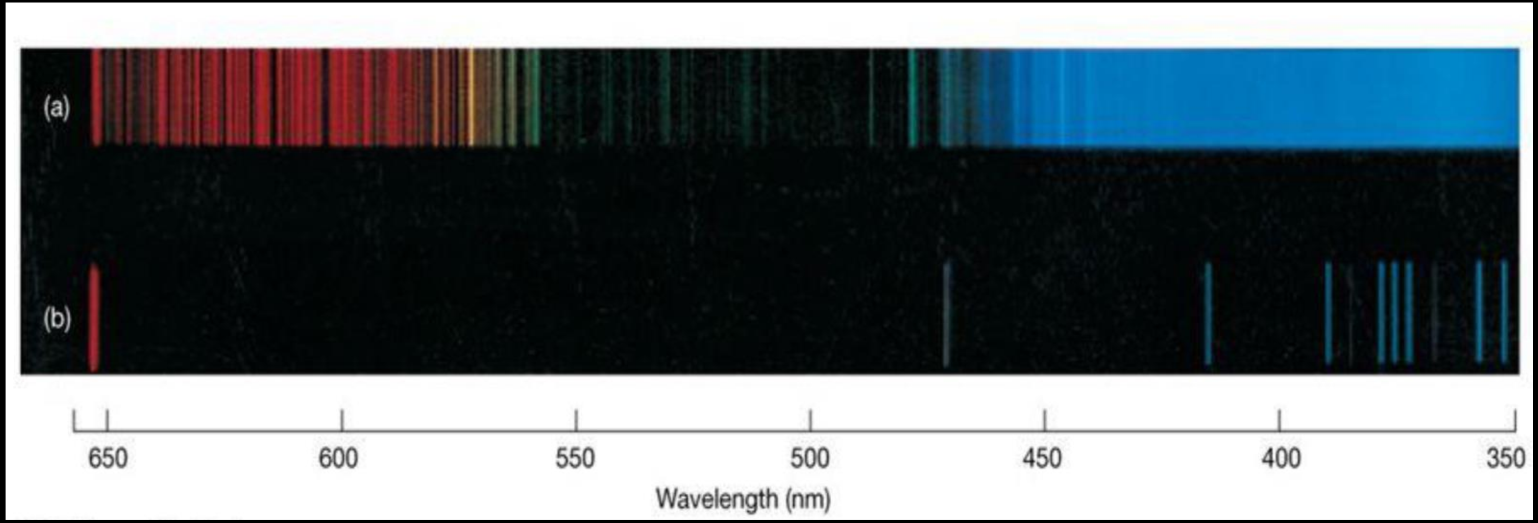


$$\hat{H}_{system} = \hat{H}_{H} + \hat{H}_{rest-of-atoms} + V_{\text{int}}$$

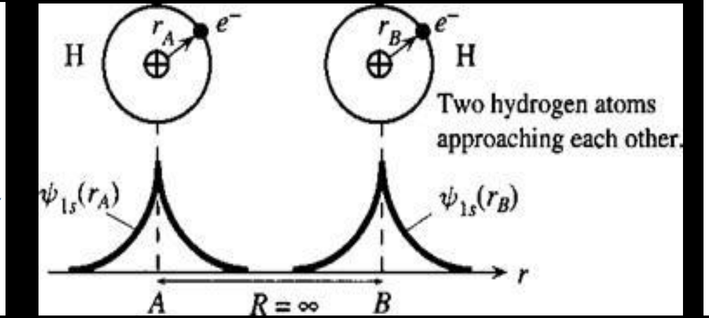
Although everything fits properly with what we know previously, let’s consider all these in more detail…

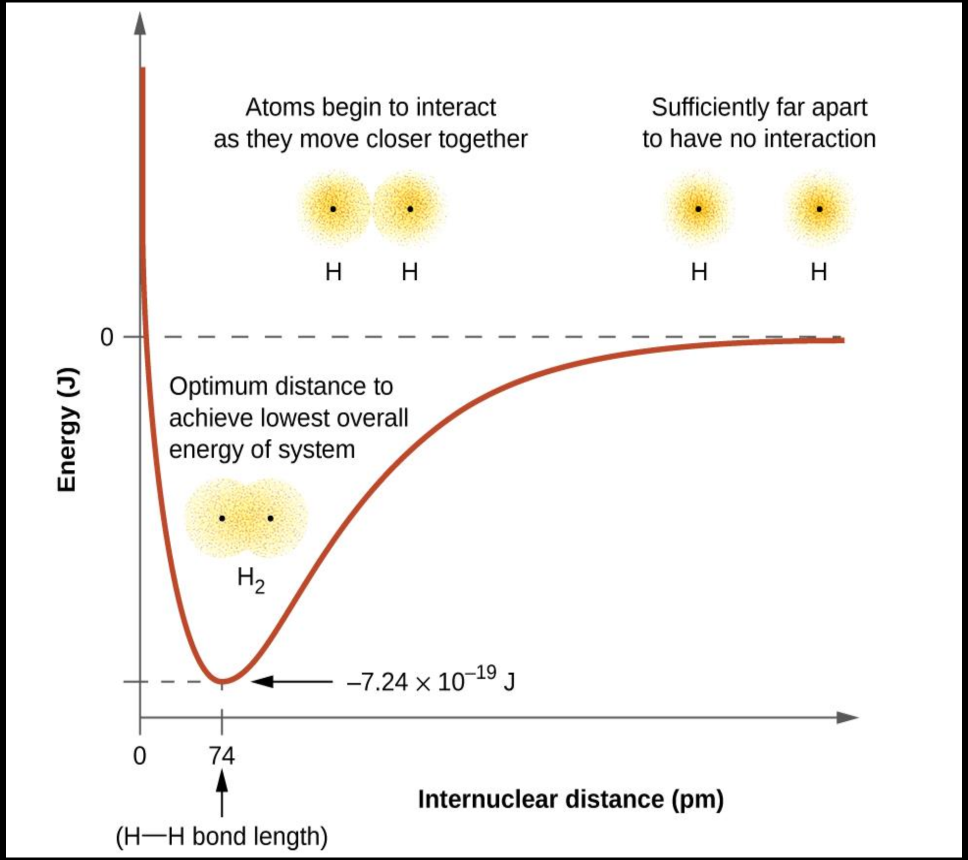
Let’s assume because of diffusion there are two hydrogen atoms in the cavity and reconsider the spectrum





Obviously, the new spectrum is not a simple shift of hydrogen atom’s spectrum and whole idea of using $\hat{V}_{environment}$ fails…





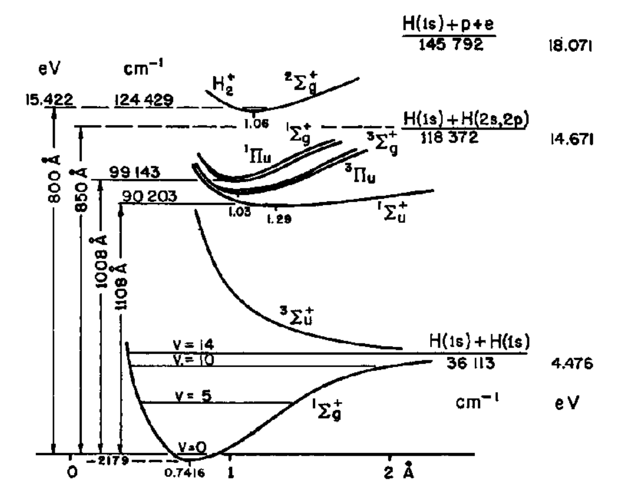
The same general strategy of dividing into system plus environment works but now the system is the trapped hydrogen molecule and the whole analysis could be redone

$$\hat{H}_{trapped-H_2} = \hat{H}_{H_2} + \hat{V}_{environment}$$

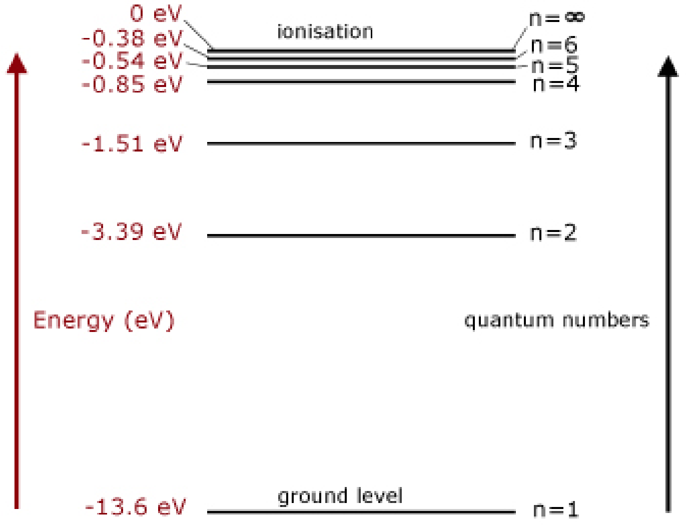
$$system\ (H_2 + atoms) \Rightarrow quantum\ identity$$

$$environment \Rightarrow ghost\ identity$$

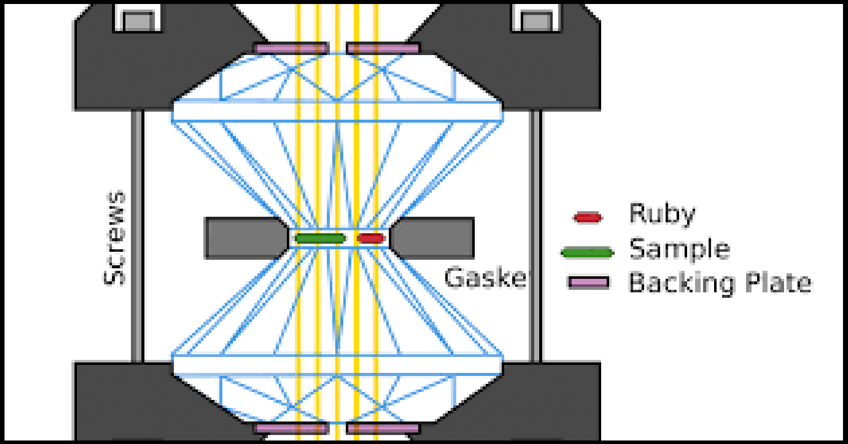
$$quantum\ subsystem \Rightarrow H_2$$



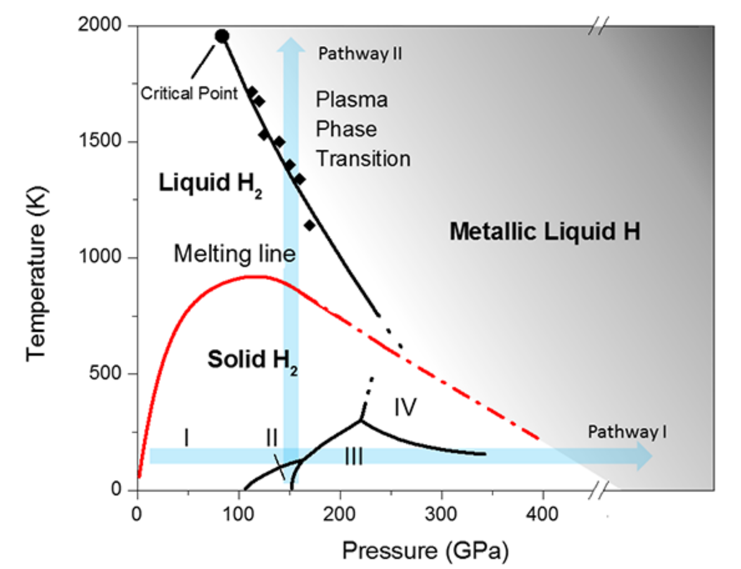
Clearly, there is no trace of the H atom's energy spectrum within the H_2 molecule's energy spectrum and seemingly no "effective Hamiltonian" may be constructed using the H atom Hamiltonian



For all practical purposes the H atoms lost their quantum identity!



Under hydrostatic pressure new phases of solid and metallic hydrogen emerges



How many electrons and protons must be taken into account for the Hamiltonian of the metallic phase? 10^2, 10^3 or maybe 10^{23} particles?

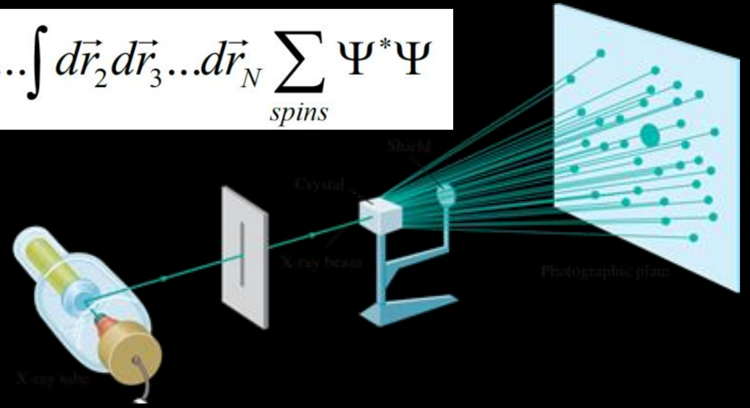
$$\hat{H}_{trapped-hydrogen} = \hat{H}_{?} + \hat{V}_{\text{diamond anvil}}$$

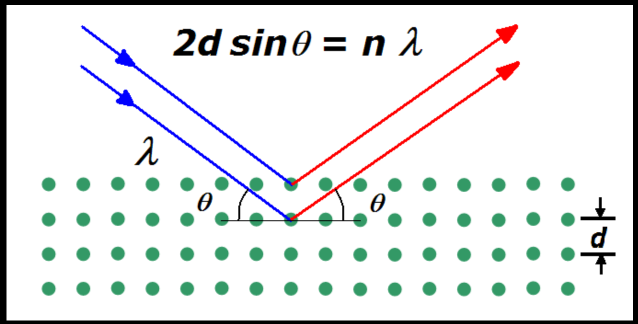
Take home lesson: As far as it goes, it seems that discerning the *system*, *environment* and *subsystem* in real-life situations is not a trivial act and is more or less driven by “empirical” facts rather than “theory”

However, and in contrast to empirical success of this scheme, the enigma of the **lost identities of atoms** is annoying and against the phenomenological atomic theory…

The common reaction of most theoreticians to this enigma is dismissing the atomic theory and claiming that indeed atoms in molecules lost their quantum identity and only real physical systems are those having their own Hamiltonian and Hilbert space/subspace

$$\rho(\vec{r}) = N\int\ldots\int d\vec{r}_2 d\vec{r}_3\ldots d\vec{r}_N \sum_{spins}\Psi^*\Psi$$



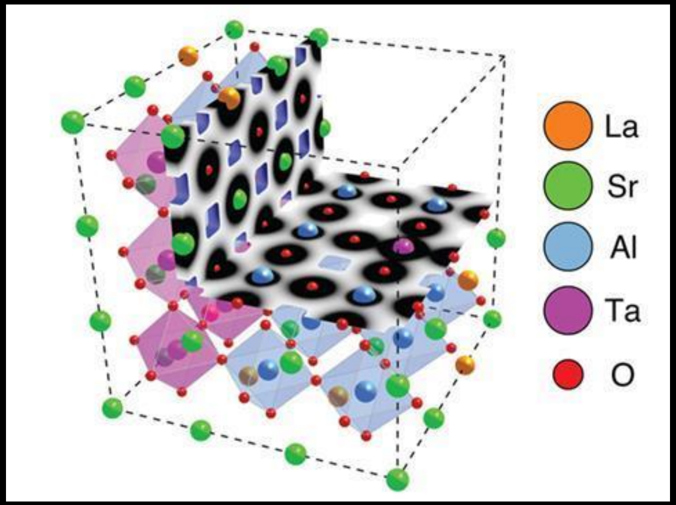


$$Generalized \Rightarrow M_{molecule}(\vec{r}) \approx \sum_i M_{i,free-atom}(\vec{r})$$

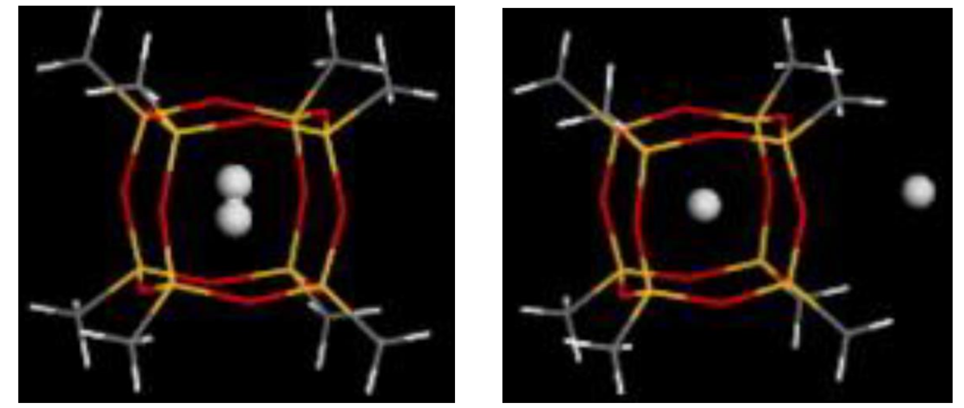
$$\rho_{molecule}(\vec{r}) \approx \sum_i \rho_{i,free-atom}(\vec{r})$$

The only problem with this viewpoint is that it is against experimental facts!

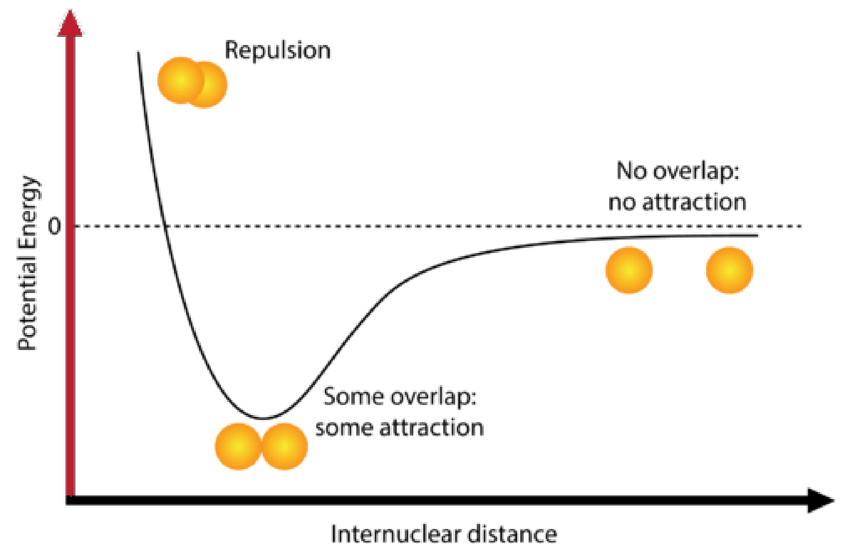
Indeed, experimentalists are able to discern the atomic composition of matter using various spectroscopic, thermodynamic, chemical, etc. measurements and interpreting them with atomic models



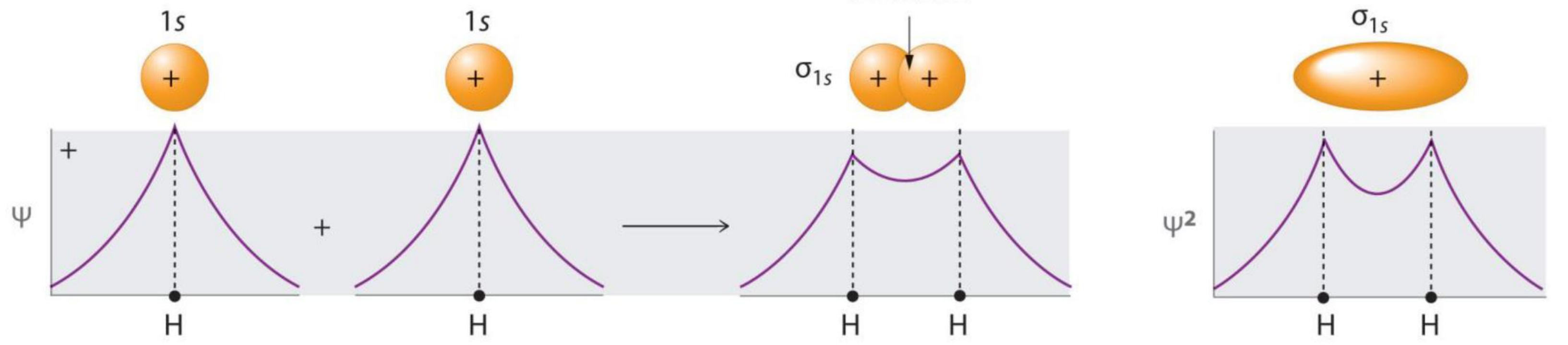
Let’s have a gedanken experiment

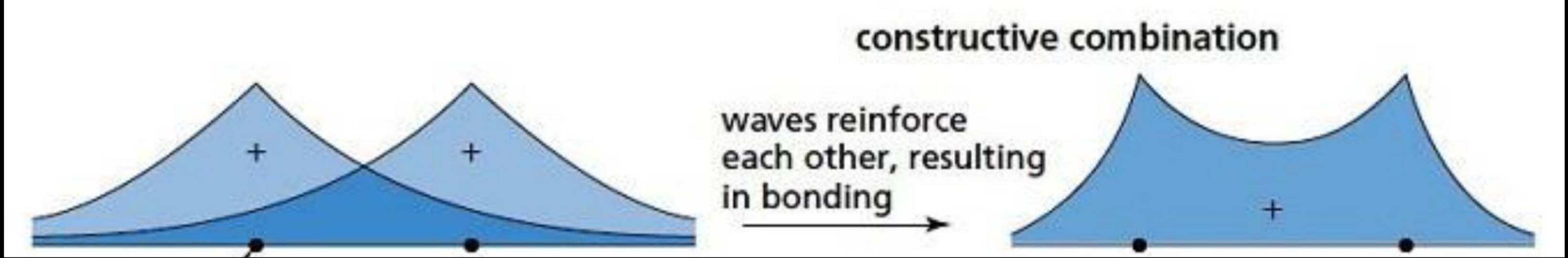


If the two hydrogen atoms are sufficiently apart: $\hat{H}_{system} = \hat{H}_{H_A} + \hat{H}_{H_B} + V_{\text{int}}(A,B)$, while in the vicinity of equilibrium distance: $\hat{H}_{system} = \hat{H}_{H_2}$. When this transition is taking place?



Clearly, there is no sharp transition!





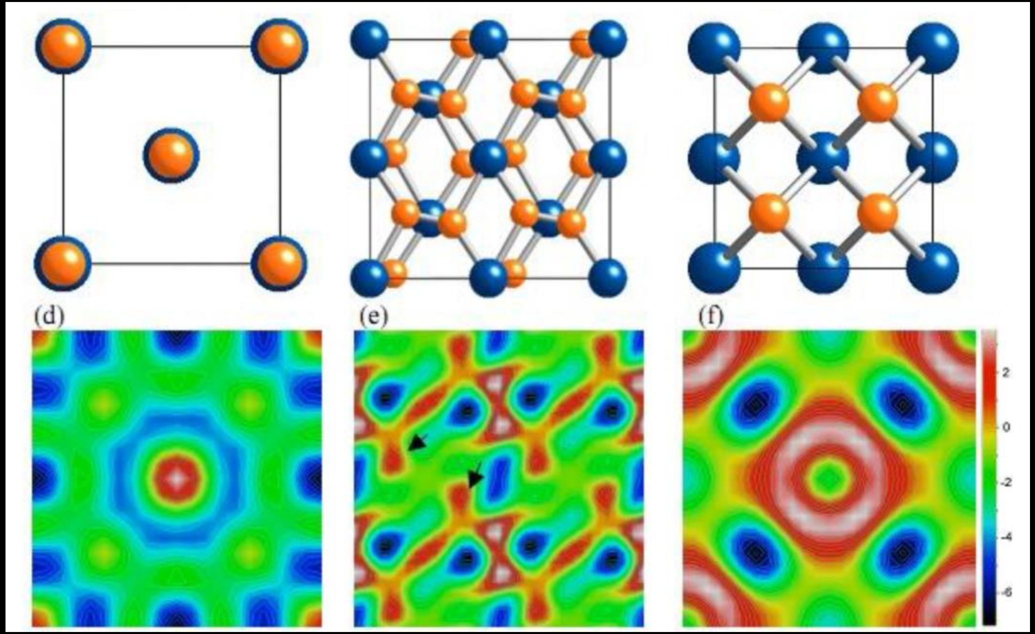
If a certain degree of freedom or a cluster of particles is “sufficiently” uncoupled from the rest of system it deserved to have its own Hamiltonian and Hilbert space and so also deserved to be called a quantum subsystem

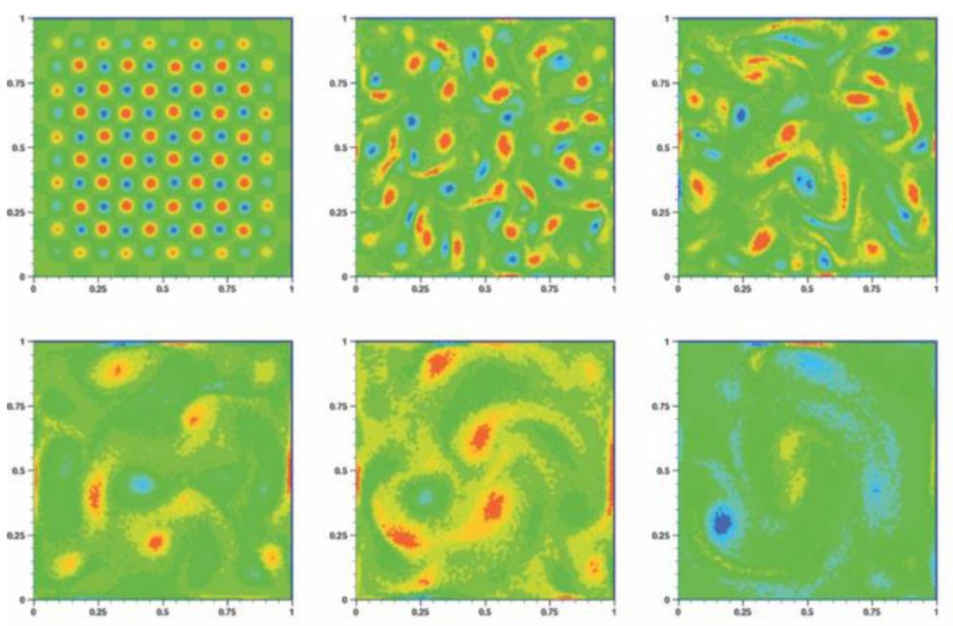
However, the word “sufficient” has a more or less “subjective” nature and it is usually possible to conceive “continuous” transitions that the subsystem lost its identity

Losing the identity as a quantum subsystem does *not* imply that the corresponding degree of freedom or the cluster are unrecognizable within the system

Usually, the property densities and the expectation values of the observables of the system is re-constructible from the free subsystems:

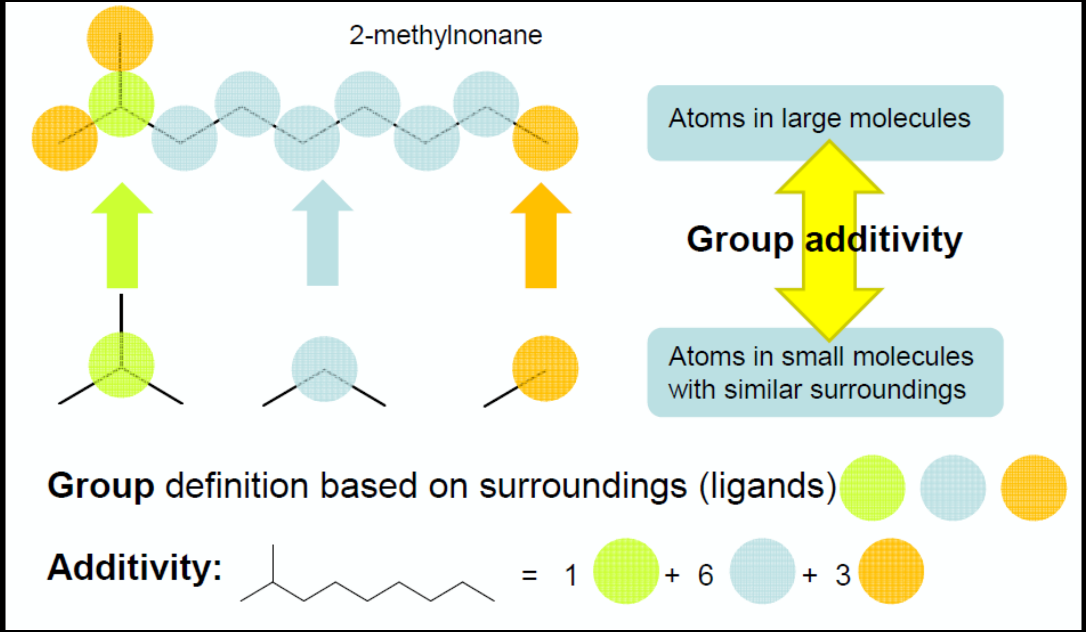
$$M_{system}(\vec{r}) \approx \sum_i M_{i,free-subsystem}(\vec{r}), \qquad \langle M_{system} \rangle \approx \sum_i \langle M_{i,free-subsystem} \rangle$$





Vorticity

$$\omega(\vec{r},t)=\nabla\times\vec{u}(\vec{r},t)$$



2-methylnonane

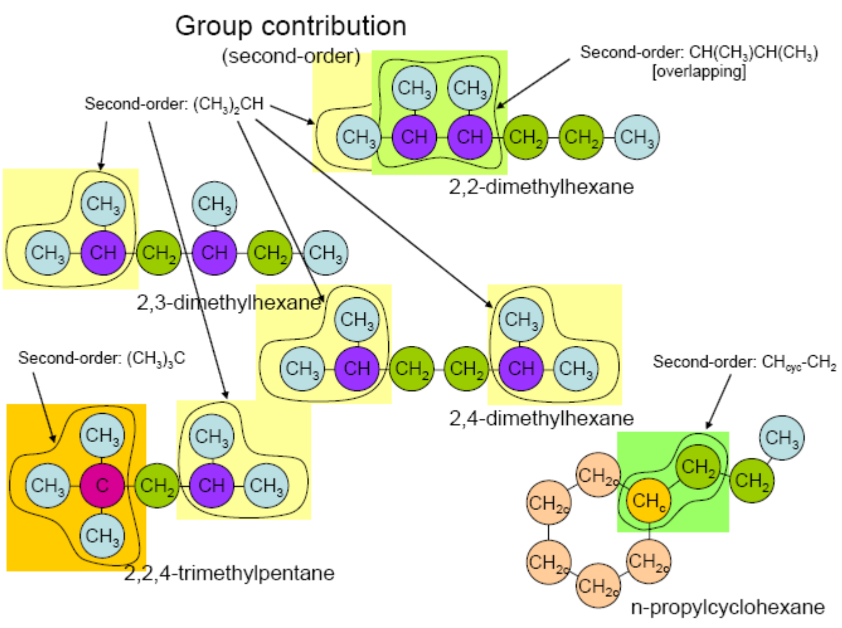
Atoms in large molecules

Group additivity

Atoms in small molecules with similar surroundings

Group definition based on surroundings (ligands)

Additivity: = 1 ● + 6 ● + 3 ●



Group contribution (second-order)

Second-order: CH(CH$_3$)CH(CH$_3$) [overlapping]

Second-order: (CH$_3$)$_2$CH

Second-order: (CH$_3$)$_3$C

Second-order: CH$_{cyc}$-CH$_2$

2,2-dimethylhexane

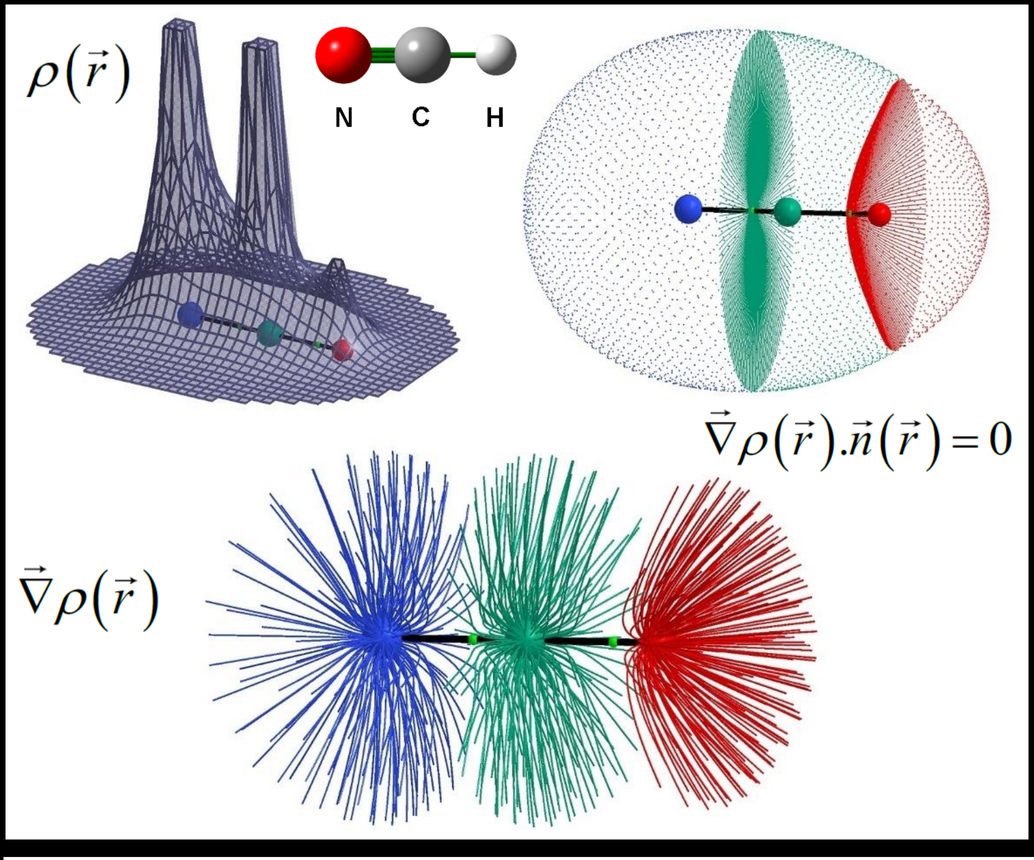
2,3-dimethylhexane

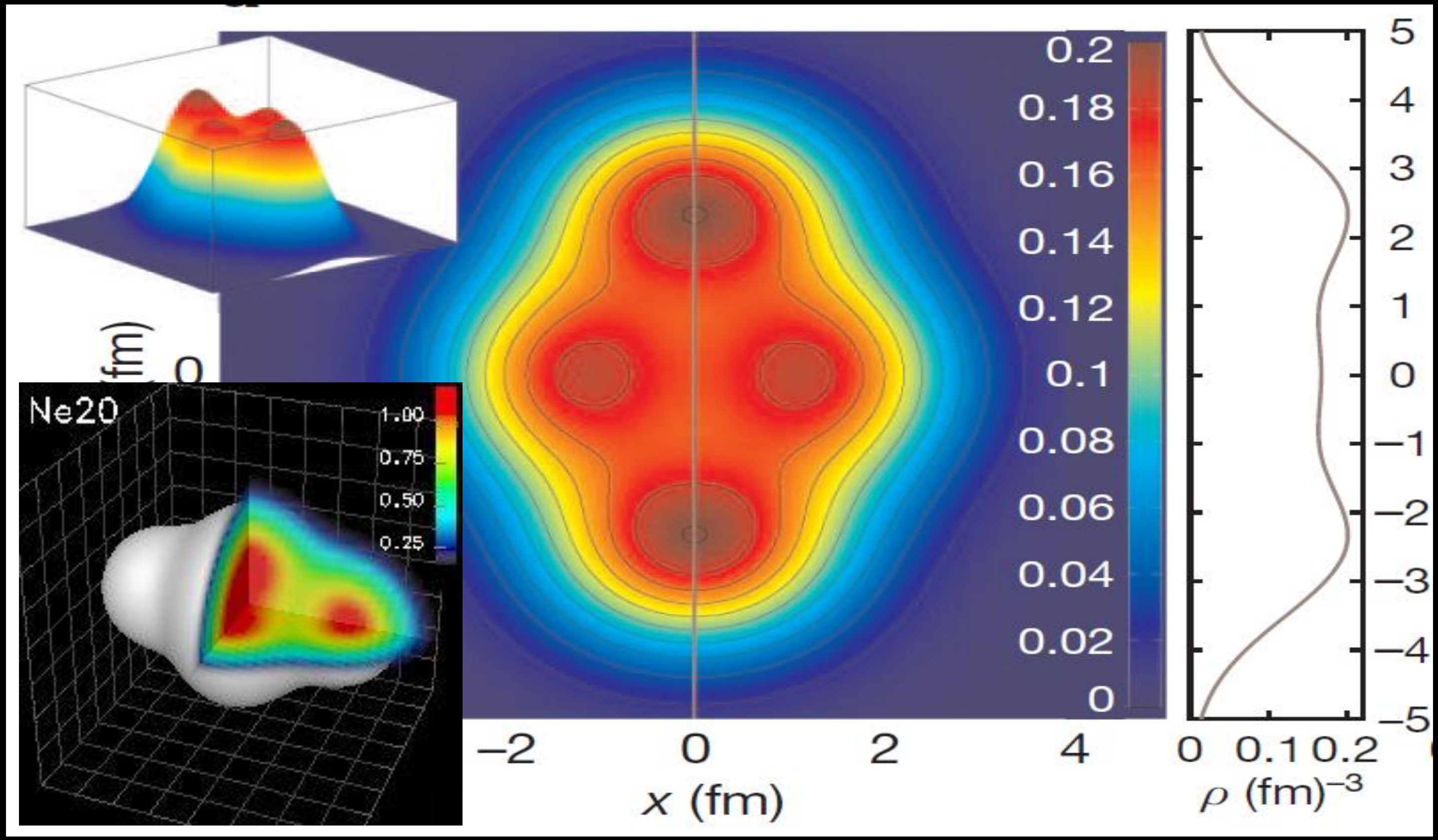
2,4-dimethylhexane

2,2,4-trimethylpentane

n-propylcyclohexane

It seems bonded atoms are perturbed enough not to be conceived as quantum subsystems but recognizable enough to be conceived as a “new kind” of subsystems



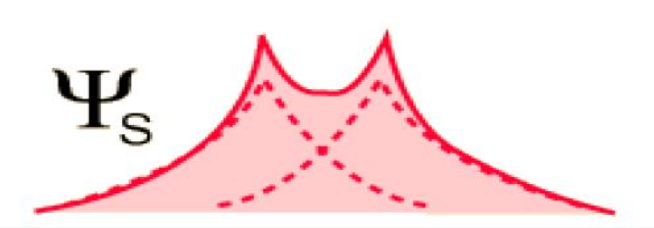


$$\hat{M} \Rightarrow M_{system}(\vec{r}) \quad \xrightarrow{\int M_{system}(\vec{r})d\vec{r} = \langle\hat{M}\rangle} \quad \left\langle\hat{M}\right\rangle = \sum_i \int M(\vec{r})d\vec{r} = \sum_i M(subsystem,i)$$

$M(subsystem,i) \Rightarrow$ Nicely fits to experimental group additivities

$M_{system}(\vec{r}) \Rightarrow$ They usually contain the same subsystem “patterns”

observed is electron density



$$\sigma_{\Omega} = \left\langle N^2\right\rangle_{\Omega} - \left\langle N\right\rangle_{\Omega}^2 > 0$$

$\sigma_{R^3} = 0$,closed system

$$L\left[\Psi,\vec{\nabla}\Psi\right]=\int L(\vec{r})d\vec{r},$$
$$L(\vec{r})=\int d\vec{r}_2\ldots\int d\vec{r}_N\left\{\left(-\hbar^2/2m_e\right)\vec{\nabla}\Psi^*\cdot\vec{\nabla}\Psi-V\Psi^*\Psi\right\}$$

$$\delta_{\Psi/\Psi^*}L=0\Rightarrow\left\{\left(-\hbar^2/2m_e\right)\nabla^2\Psi+V\Psi\right\}=E\Psi,cc$$

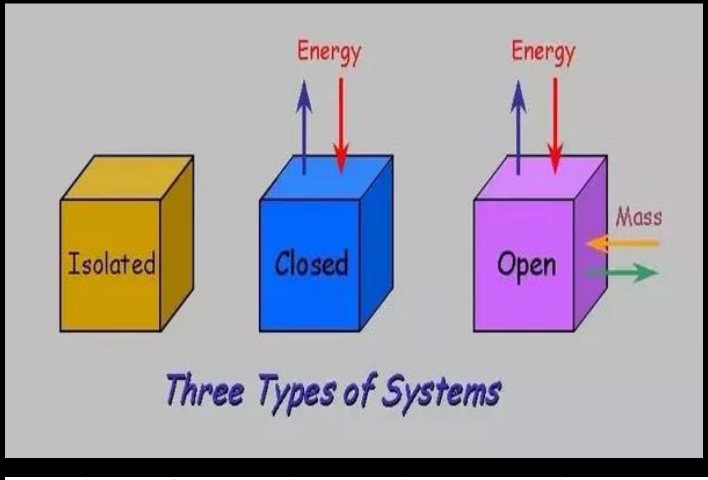
$$L\left[\Psi,\vec{\nabla}\Psi,\Omega\right]=\int_{\Omega}L(\vec{r})d\vec{r},\ \hat{H}\Psi=E\Psi,\ \delta\Psi=-\varepsilon\left(i/\hbar\right)\hat{G}$$
$$\delta_{\Psi}L=-(\varepsilon/2)\left\{\oint_{\partial\Omega}dS\,\vec{J}_G(\vec{r})\cdot\vec{n}(\vec{r})+cc\right\}+\left(-\hbar^4/4m_e\right)\int_{\Omega}\nabla^2\rho(\vec{r})d\vec{r}$$

$$\vec{J}_G(\vec{r})=\left(\hbar/2m_e i\right)\int d\vec{r}_2\ldots\int d\vec{r}_N\left\{\Psi^*\vec{\nabla}\left(\hat{G}\Psi\right)-\left(\vec{\nabla}\Psi^*\right)\left(\hat{G}\Psi\right)\right\}$$

$$\int_{\Omega}\nabla^2\rho(\vec{r})d\vec{r}=\oint_{\partial\Omega}dS\,\vec{\nabla}\rho(\vec{r})\cdot\vec{n}(\vec{r})$$

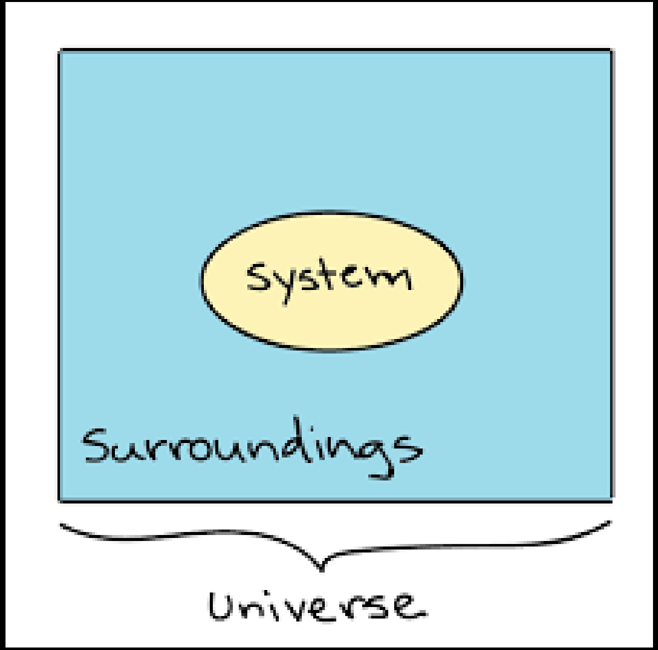
Evidently, these subsystems do not obey the variational principle of the system, but yet there are distinct because of the non-zero “surface” term; they are called *real-space open quantum subsystems*

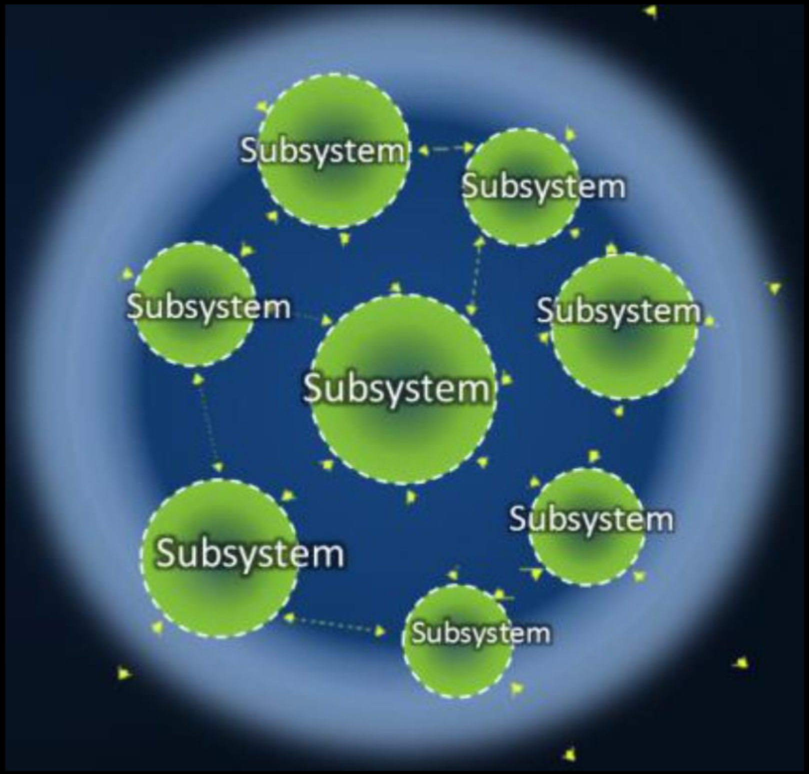
Prepared by Shant Shahbazian for the conference "The imporatnt role of the fundational physics in the future evolution of science" held at the Institute for research in fundamental sciences (IPM) (19-Dec-2017)



$$\overbrace{\underline{\text{isolated}}\ \text{system}}^{\text{Hamiltonian, Hilbert space}} \Rightarrow \overbrace{\underline{\text{closed}}\ \text{subsystem}}^{\substack{\text{Hamiltonian of subsystem +}\\ \text{environment (effective}\\ \text{potenetial or bath), Hilbert space}}} \Rightarrow \overbrace{\underline{\text{real}-\text{space open}}\ \text{subsystem}}^{\substack{\text{no Hamiltonian or independent Hilbert space,}\\ \text{patterns in real}-\text{space densities, share of}\\ \text{expectation values and non}-\text{zero currents}\\ \text{at real}-\text{space boundaries}}}$$

The fact that the real-space open subsystems do *not* have their own variational principle points to the fact that their state is dictated by the variational principle governed the system, in other words, subsystems are exchanging energy and particles to make the energy of the whole system minimized and this is different from the idea of infinite bath which is not affected by encompassing subsystem





Let’s just ask some questions at the end!

Does every system in nature is governed by a variational principle?

Does every system in nature is describable by a Hamiltonian or a Lagrangian?

Is there a sound theoretical route to a universal definition of system, environment and subsystem?

What is a system?

Thanks for your attention