Independent electrons in an effective potential

Quantum Mechanics

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are 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, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.A.M. Dirac,
Quantum Mechanics of Many-Electron Systems
Proc. Royal Soc. 129, 714 (1929).

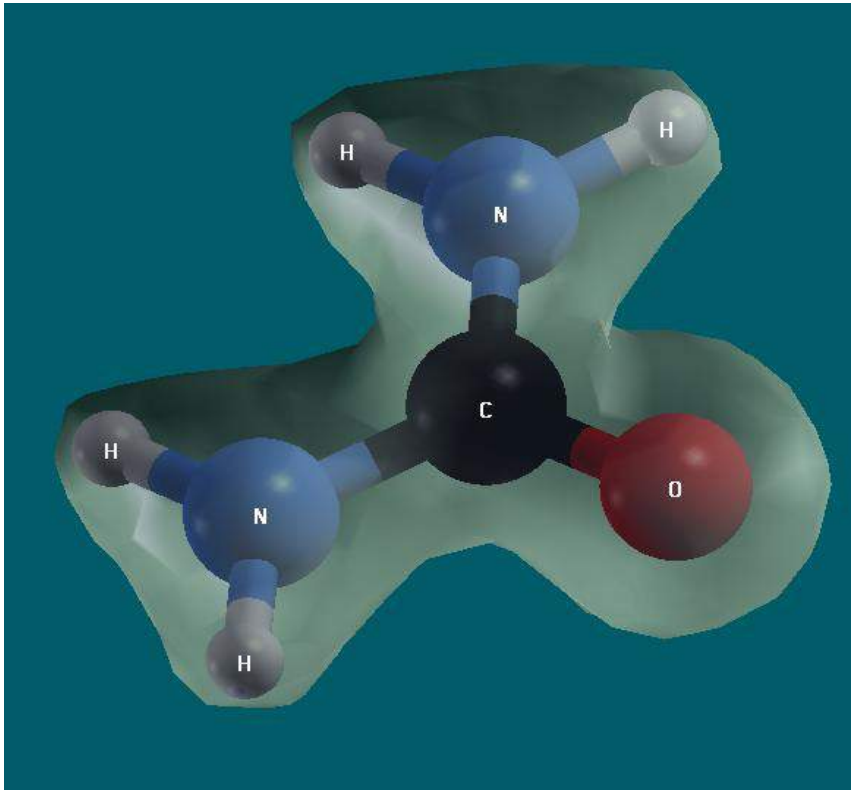
Adiabatic approximation

Independent electrons in an effective potential

Hartree–Fock

Density Functional Theory

MBPT - GW



Adiabatic Approximation

$$[T_I + T_e + W_{eI} + W_{ee} + W_{II}]\,\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad M_I >> m_e$$

The slow nuclei move in the potential energy surface (PES) generated by the fast electrons

$$\begin{cases} [T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi_0(\mathbf{r}|\mathbf{R}) = E_{GS}(\mathbf{R})\;\Phi_0(\mathbf{r}|\mathbf{R}) \\ M_I \ddot{R}_I = F_I(\mathbf{R}) = -\nabla_{R_I} E_{GS}(\mathbf{R}) \end{cases}$$

The GS PES is the most important one.
Classical Mechanics is often adequate to describe ions.

Independent electrons in an effective potential

$$[T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi_0(\mathbf{r}|\mathbf{R}) = E_{GS}(\mathbf{R})\;\Phi_0(\mathbf{r}|\mathbf{R})$$

The solution of the electronic problem is still daunting

$\Phi_0(\mathbf{r}|\mathbf{R})$ is an (antisymmetric) function of $3N_{el}$ real variables + spin

even storing a wfc for Oxygen dimer (16 el) with merely 10 entries per coordinate would require $8 \times 10^{48}\ bytes$

$(Marconi \approx 17 \times 10^3\ Tbytes)$ $\qquad 8 \times 10^{36}\ Tbytes$

Independent electrons in an effective potential

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{2}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{e^2}{2}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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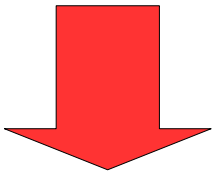


$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\vec{r},\mathbf{R})\right]\phi_i(\vec{r}) = \varepsilon_i\,\phi_i(\vec{r})$$

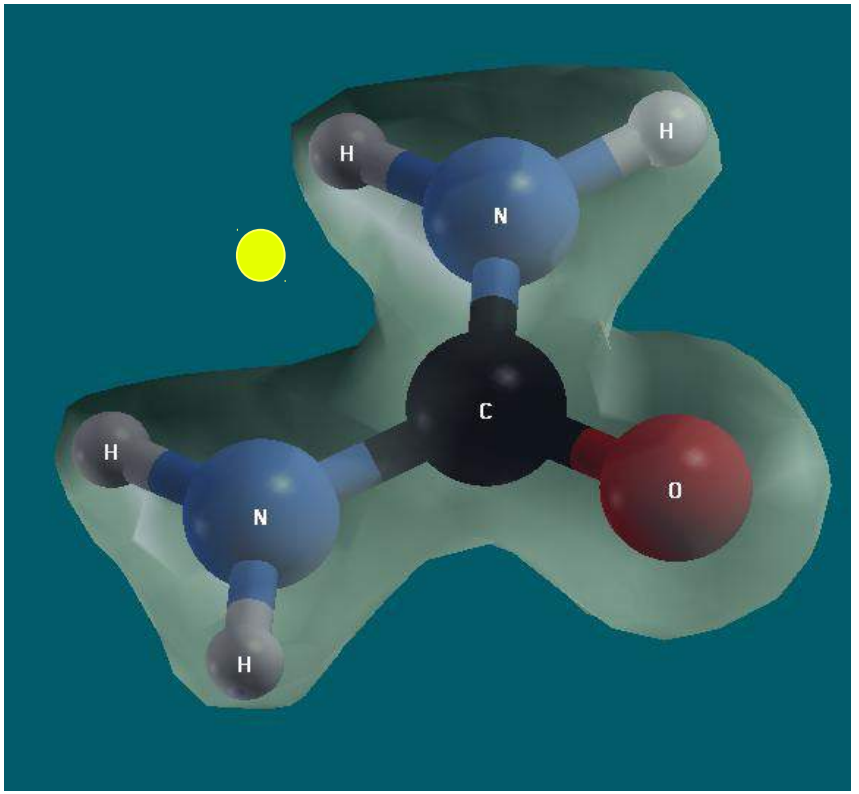
Why is it a good (or at least decent) idea ?

Independent electrons in an effective potential

The electrostatic potential felt by a *test* -e charge is therefore

$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Given a system of ions and electrons its GS electronic density n(r) is well defined (although not easy to compute)

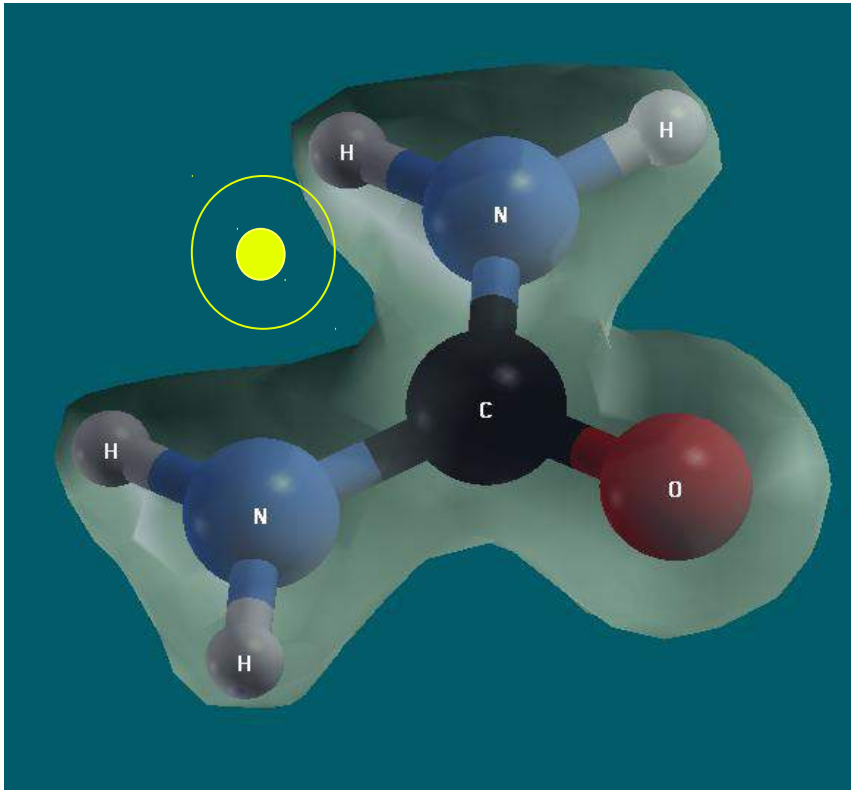


Independent electrons in an effective potential

The electrostatic potential felt by a *real* -e charge is instead

$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}') + \delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

because electrons *readjust* so as to avoid the extra charge.

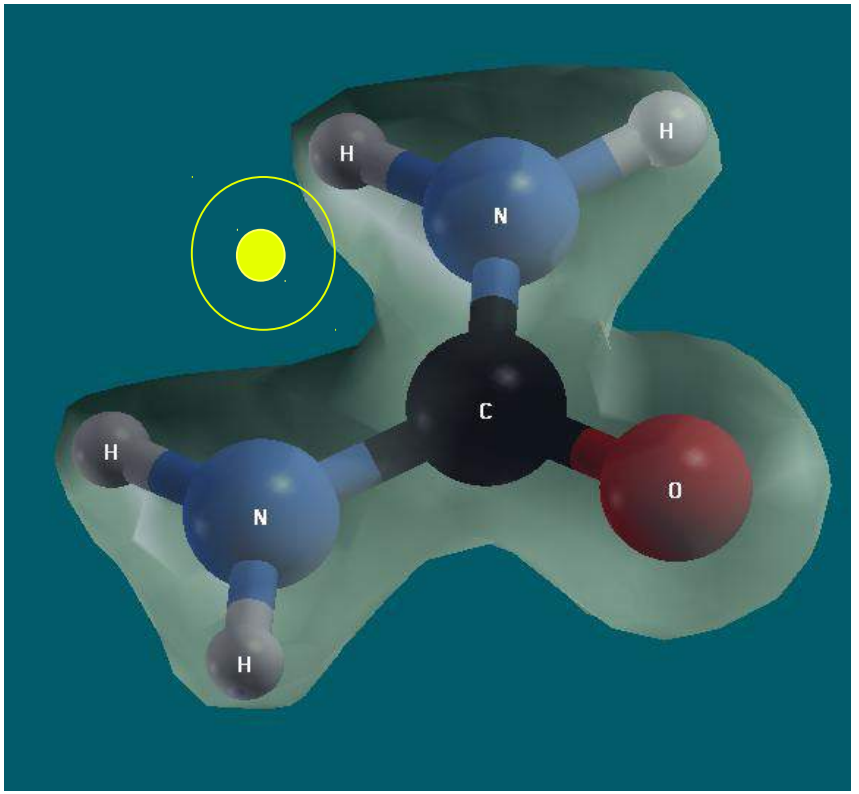


Independent electrons in an effective potential

The electrostatic potential felt by a *real* -e charge is instead

$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{scr}(\mathbf{r})$$

because electrons *readjust* so as to avoid the extra charge and *screen* the perturbation.



Independent electrons in an effective potential

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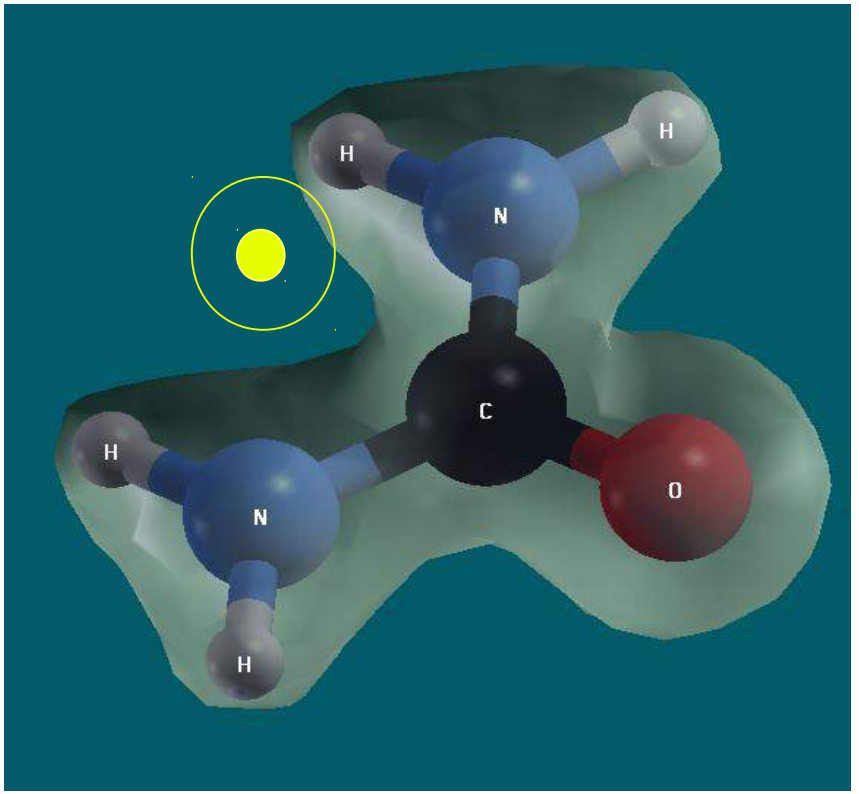
A negative muon ($m_\mu \approx 200 m_e$) would move in this potential.

$$\left[T_\mu + V_{eff}(\mathbf{r})\right] \xi_\mu(\mathbf{r}) = \varepsilon_\mu \, \xi_\mu(\mathbf{r})$$

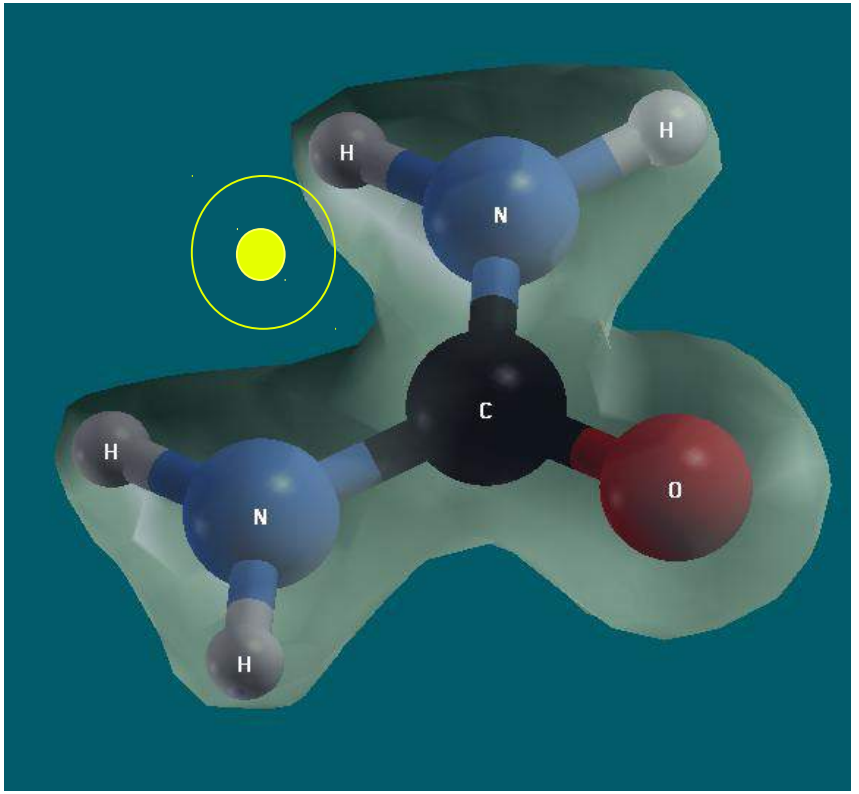


indeed ...

$$[T_I + T_\mu + T_e + W_{eI} + W_{ee} + W_{II} + W_{e\mu} + W_{I\mu}]\,\Psi = E\Psi$$

$$\Psi(\mathbf{r}, r_\mu, \mathbf{R}) = \Phi(\mathbf{r}|r_\mu, \mathbf{R})\;\xi(r_\mu|\mathbf{R})\;\chi(\mathbf{R})$$

AA: $\quad T_I\Phi\xi\chi \;\approx\; \Phi\xi\, T_I\chi, \qquad T_\mu\Phi\xi \;\approx\; \Phi\, T_\mu\xi$



$$[T_I + T_\mu + T_e + W_{eI} + W_{ee} + W_{II} + W_{I\mu} + W_{e\mu}]\,\Psi = E\Psi$$

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AA: $\quad T_I\Phi\xi\chi \;\approx\; \Phi\xi\, T_I\chi, \qquad T_\mu\Phi\xi \;\approx\; \Phi\, T_\mu\xi$

$$\frac{T_I\chi(\mathbf{R})}{\chi(\mathbf{R})} + \frac{T_\mu\xi(r_\mu|\mathbf{R})}{\xi(r_\mu|\mathbf{R})} + \frac{[T_e + W_{eI} + W_{ee} + W_{II} + W_{I\mu} + W_{e\mu}]\Phi(\mathbf{r}|r_\mu, \mathbf{R})}{\Phi(\mathbf{r}|r_\mu, \mathbf{R})} = E$$

function of r_μ & $\mathbf{R}$ $\quad\Rightarrow\quad$ function of r_μ & $\mathbf{R}$ $\quad$ let's call it $E(\mathbf{R}) + V_{eff}(r_\mu|\mathbf{R})$

Where $E(\mathbf{R})$ is the solution w/o $W_{I\mu}$ and $W_{e\mu}$

$$\underbrace{\frac{T_I\chi(\mathbf{R})}{\chi(\mathbf{R})}+\frac{T_\mu\xi(r_\mu|\mathbf{R})}{\xi(r_\mu|\mathbf{R})}}_{\text{function of } r_\mu \,\&\, \mathbf{R}} + \underbrace{\frac{[T_e+W_{eI}+W_{ee}+W_{II}+W_{e\mu}+W_{I\mu}]\Phi(\mathbf{r}|r_\mu,\mathbf{R})}{\Phi(\mathbf{r}|r_\mu,\mathbf{R})}}_{\text{function of } r_\mu \,\&\, \mathbf{R}} = E$$

$\Rightarrow$ let's call it $E(\mathbf{R})+V_{eff}(r_\mu|\mathbf{R})$

$$\underbrace{\frac{T_I\chi(\mathbf{R})}{\chi(\mathbf{R})}}_{\text{function of } \mathbf{R}} + \underbrace{\frac{T_\mu\xi(r_\mu|\mathbf{R})}{\xi(r_\mu|\mathbf{R})}+E(\mathbf{R})+V_{eff}(r_\mu|\mathbf{R})}_{\text{function of } \mathbf{R}} = E$$

$\Rightarrow$ let's call it $E(\mathbf{R})+\varepsilon_\mu(\mathbf{R})$

$$\left[-\frac{\hbar^2}{2m_\mu}\nabla_\mu^2 + \cancel{E(\mathbf{R})} + V_{eff}(r_\mu|\mathbf{R})\right]\xi(r_\mu|\cancel{\mathbf{R}}) = (\cancel{E(\mathbf{R})}+\varepsilon_\mu(\cancel{\mathbf{R}}))\,\xi(r_\mu|\cancel{\mathbf{R}})$$

$$\left[-\frac{\hbar^2}{2m_\mu}\nabla^2_\mu + V_{eff}(r_\mu|\mathbf{R})\right]\xi(r_\mu) = \varepsilon_\mu\,\xi(r_\mu)$$

$$E(\mathbf{R})+V_{eff}(r_\mu|\mathbf{R}) = \frac{[T_e+W_{eI}+W_{ee}+W_{II}+W_{I\mu}+W_{e\mu}]\Phi(\mathbf{r}|r_\mu,\mathbf{R})}{\Phi(\mathbf{r}|r_\mu,\mathbf{R})}$$

$$E(\mathbf{R})+V_{eff}(r_\mu|\mathbf{R}) = \langle\Phi\,|T_e+W_{eI}+W_{ee}+W_{II}+W_{I\mu}+W_{e\mu}|\Phi\rangle$$

if $\qquad \mathcal{H}_\lambda = T_e+W_{eI}+W_{ee}+W_{II}+\lambda\,(W_{I\mu}+W_{e\mu})$

$$\lambda = 0\ :\ E(\mathbf{R}) \qquad\qquad \lambda = 1\ :\ E(\mathbf{R}) + V_{eff}(r_\mu|\mathbf{R})$$

$$E(\mathbf{R}) + V_{eff}(r_\mu|\mathbf{R}) = E(\mathbf{R}) + \int_0^1 d\lambda\,\langle\Phi^{el}_\lambda\,|W_{I\mu}+W_{e\mu}|\Phi^{el}_\lambda\rangle$$

$$V_{eff}(r_\mu|\mathbf{R}) = \int_0^1 d\lambda\,\langle\Phi^{el}_\lambda\,|W_{I\mu}+W_{e\mu}|\Phi^{el}_\lambda\rangle$$

$$\left[-\frac{\hbar^2}{2m_\mu}\nabla_\mu^2 + V_{eff}(r_\mu|\mathbf{R})\right]\xi(r_\mu) = \varepsilon_\mu\,\xi(r_\mu)$$

$$V_{eff}(r_\mu|\mathbf{R}) = \int_0^1 d\lambda \left\langle \Phi_\lambda^{el} \left| W_{I\mu} + W_{e\mu} \right| \Phi_\lambda^{el} \right\rangle$$

$$V_{eff}(r_\mu|\mathbf{R}) = W_{I\mu} + \int_0^1 d\lambda \left\langle \Phi_\lambda^{el} \left| W_{e\mu} \right| \Phi_\lambda^{el} \right\rangle$$

$$= V_{eI}(r_\mu|\mathbf{R}) + e^2 \int_0^1 d\lambda \int \frac{n_\lambda(r')}{|r' - r_\mu|} dr'$$

$$= V_{eI}(r_\mu|\mathbf{R}) + e^2 \int \frac{n(r')}{|r' - r_\mu|} dr' + e^2 \int_0^1 d\lambda \int \frac{\delta n_\lambda(r')}{|r' - r_\mu|} dr'$$

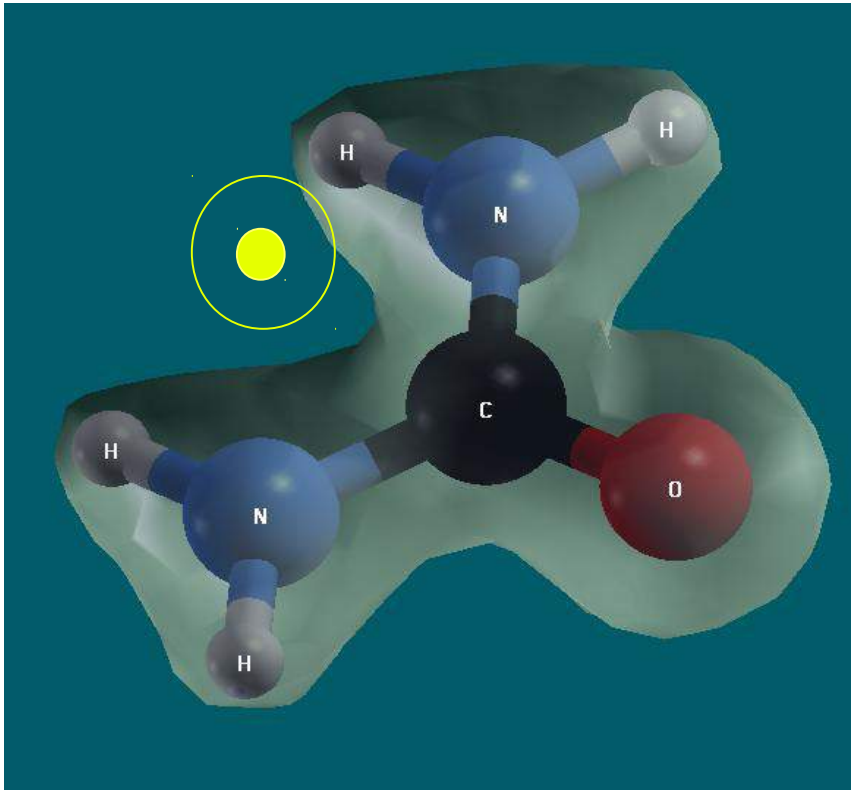
where the last term describes static screening

Independent electrons in an effective potential

$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{scr}(\mathbf{r})$$

A negative muon ($m_\mu \approx 200 m_e$) moves in this potential.

$$\left[T_\mu + V_{eff}(\mathbf{r})\right] \xi_\mu(\mathbf{r}) = \varepsilon_\mu \, \xi_\mu(\mathbf{r})$$



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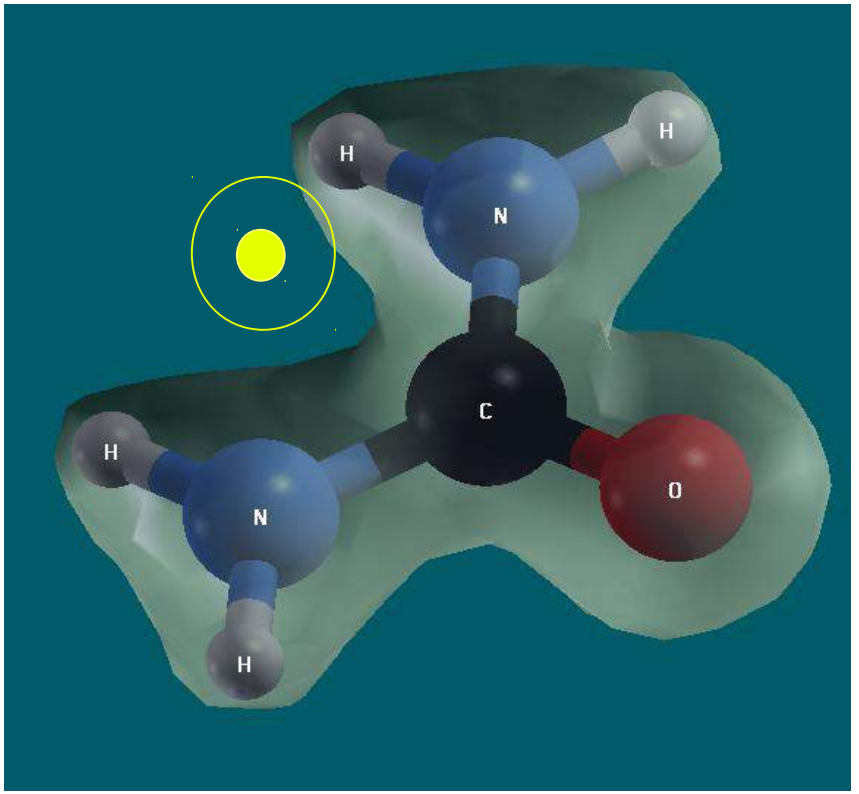
$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r},\mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{scr}(\mathbf{r})$$

We can imagine that electrons themselves will behave the same

$$\left[T_e + V_{eff}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \, \phi_i(\mathbf{r})$$

including *dynamical* screening and Pauli principle (exchange) effects.



Independent electrons in an effective potential

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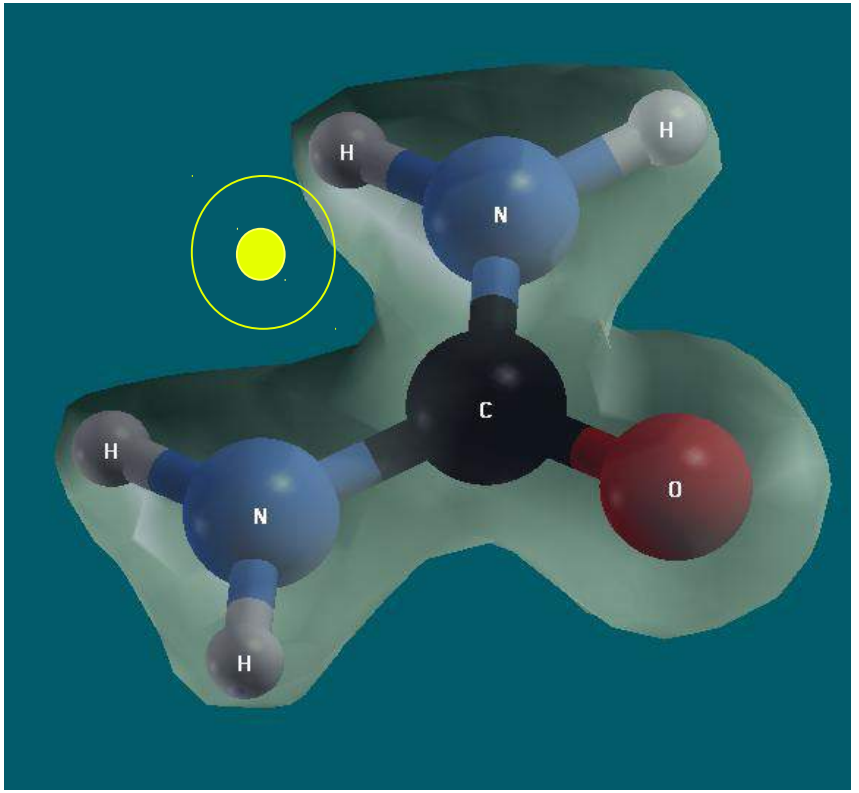
The external potential is $\mathcal{O}(Z_{tot})$

The Hartree potential is $\mathcal{O}(N_{el})$

The screening potential is $\mathcal{O}(1)$



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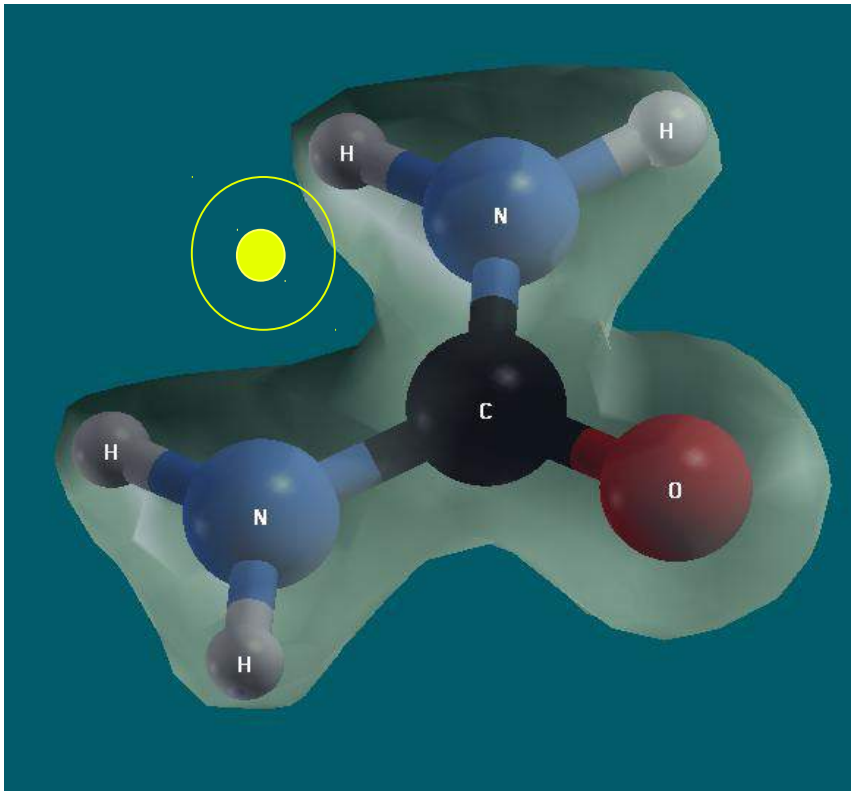
$$V_{eff}(\mathbf{r}) = V_{eI}(\mathbf{r},\mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{scr}(\mathbf{r})$$

$$\left[T_e + V_{eff}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \, \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2 \sum_i |\phi_(\mathbf{r})|^2$$

self-consistent
single-particle
set of equations

ex: HF, DFT, GW, ...



about your cat Mr. Schroedinger I have good news and bad news

THE END


Scuola Internazionale Superiore di Studi Avanzati
«tra poi seguir virtute e conoscenza»