

# Factorisation of molecular states and Born-Oppenheimer approximation.

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## Introduction

This talk is based on the following works :

→ Th. Jecko, B.T. Sutcliffe, R.G. Woolley. *On factorization of molecular wavefunctions*.  
J. Phys. A : Math. Theor. 48, (2015), 445201 (20pp). Available on :

“ *[http : //arxiv.org/abs/1506.00103](http://arxiv.org/abs/1506.00103)* ” .

→ Th. Jecko. *On the mathematical treatment of the Born-Oppenheimer approximation*.  
J. Math. Phys. 55, 053504 (2014). Available on :

“ *[http : //arxiv.org/abs/1303.5833](http://arxiv.org/abs/1303.5833)* ” .

## Outline

- Molecular Hamiltonian.
- Review of the Born-Oppenheimer approximation.
- Factorisation of bound states.
- Discussion and open questions.

## Molecular Hamiltonian

We consider a molecular Hamiltonian without the mass centre motion :

$$H = -\nabla_R^T \cdot M \cdot \nabla_R + H_{el}(R),$$

where  $R$  denotes the nuclear variables,  $H_{el}(R)$  is the electronic hamiltonian at nuclear positions  $R$ , and  $M$  is a positive matrix containing the (inverse) nuclear masses. The interaction between particles is given by the Coulomb potential.

We are interested in bound states for  $H$ , i.e. *square integrable* functions  $\Psi$  satisfying  $H\Psi = E\Psi$  for some real  $E$ . Note that the usual derivatives of  $\Psi$  may be ill-defined.

## Born-Oppenheimer approximation

We present here the mathematical point of view of the Born-Oppenheimer approximation.

For (almost) all  $R$ ,  $H_{el}(R)$  is self-adjoint operator. Therefore it has a spectral resolution that “diagonalizes” it.

In particular, one can decompose appropriate square integrable functions  $f$  of the electronic variables in this spectral resolution :

$$f = \sum_{j=1}^N \langle g_j(r; R), f(r) \rangle_r g_j(\cdot, R) + \int_{\lambda \geq T_R} dS_R(\lambda) f,$$

where the  $g_j(\cdot, R)$  are eigenfunctions of  $H_{el}(R)$  with energies  $\lambda_j(R)$ . This can be applied to  $f = \Psi(\cdot, R)$ .

An eigenfunction  $\Psi$  of  $H$  with eigenvalue  $E < T := \inf_R T_R$  should be well approximated by

$$\Psi_a(\cdot, R) = \Pi(R)\Psi(\cdot, R) = \sum_{j \in J} \langle g_j(r; R), f(r) \rangle_r g_j(\cdot, R),$$

where  $J$  is the set of indices  $j$  such that  $\lambda_j(R) \leq E$ , for some  $R$ . For each  $R$ ,  $\Pi(R)$  is a projection. Denoting  $\Pi(R)^\perp = 1 - \Pi(R)$ ,

$$H = \Pi H \Pi + \Pi^\perp H \Pi + \Pi H \Pi^\perp + \Pi^\perp H \Pi^\perp.$$

It turns out that the operator  $\Pi H \Pi$  is a good approximation of  $H$  to compute  $E$  and  $\Psi$ .

That is the sense of the validity of the Born-Oppenheimer approximation in mathematical Physics. In Chemistry and Physics, the Born-Oppenheimer approximation is said valid if the diagonal part of  $\Pi H \Pi$  is a good approximation of  $H$  for the chosen purpose.

## Factorisation

Let us now investigate the factorisation which has recently aroused interest.

Starting from a molecular bound state  $\Psi$ , we define for (almost) all  $R$ ,

$$\chi(R) = e^{iS(R)} \left( \int |\Psi(r; R)|^2 dr \right)^{1/2} \text{ and } \varphi(\cdot; R) = \chi(R)^{-1} \Psi(\cdot; R),$$

for some arbitrary real function  $S$ . The function  $\chi$  is interpreted as a nuclear wave function and, for all  $R$ ,

$$\int |\varphi(r; R)|^2 dr = 1.$$

It was claimed that the factorisation  $\Psi = \chi\varphi$  resembles to the Born-Oppenheimer approximation.

The equation  $H\Psi = E\Psi$  is formally equivalent to the following nonlinear system of equations for the factors :

$$\left(H - \chi^{-1}(\nabla_R \chi)^T \cdot M \cdot \nabla_R - E_{el}\right)\varphi = 0,$$

$$E_{el} = E - \chi^{-1}(\nabla_R^T \cdot M \cdot \nabla_R)\chi,$$

$$E_{el}\|\varphi\|_r^2 = \left\langle \varphi, \left(H - \chi^{-1}(\nabla_R \chi)^T \cdot M \cdot \nabla_R\right)\varphi \right\rangle_r.$$

Note that one has to care about the zeros of the unknown function  $\chi$ .



## Discussion

- Link between the factorisation and the Born-Oppenheimer approximation ?
- Zeros of  $\chi$ .
- Nature of the non linear system for the factors.
- Usefulness of the non linear system ?

## Conclusion

For the moment,

- the factorisation and the Born-Oppenheimer approximation seem to be different in their spirit ;
- the non linear system seems to be harder to solve than the Schrödinger equation.

Thank you for your attention !