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Smearred Coulomb potential orbitals for the electron-nucleus mean field configuration interaction method

Patrick Cassam-Chenai*

Université Côte d'Azur, LJAD, UMR 7351, 06100 Nice, France

E-mail: cassam@unice.fr

Abstract

We propose to use the eigenfunctions of a one-electron model Hamiltonian to perform electron-nucleus mean field configuration interaction (EN-MFCI) calculations. The potential energy of our model Hamiltonian corresponds to the Coulomb potential of an infinite wire with charge Z distributed according to a Gaussian function. The time independent Schrödinger equation for this Hamiltonian is solved.

The electron-nucleus mean field configuration interaction (EN-MFCI) method permits one to obtain in a single calculation, the electronic and vibrational energy levels of a molecule, without making the ‘‘Born-Oppenheimer’’ (BO) approximation^{1,2}. In contrast, the traditional methods of Quantum Chemistry are set in the frame of this approximation. They describe electronic clouds of fixed nuclear configurations and make use of orbital basis sets centered on nuclei. The latter are not appropriate for EN-MFCI calculations and their discrepancies have been bypassed so far, only by adding off-centered orbitals. However, these additional functions introduce linear dependencies with the initial orbitals and span virtual molecular orbitals of little use for the description of low energy wave functions of the molecule. So, it appears important to develop new orbital basis sets for the EN-MFCI method, able to describe the electron cloud of oscillating nuclei in a molecular system.

We propose to use the eigenfunctions of a one-electron model Hamiltonian: $H = -\frac{\Delta}{2m} + V(\vec{r})$, with a potential of the form:

$$V(\vec{r}) = -Z \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} \frac{\exp[-az_0^2]}{\|\vec{r} - \vec{r}_{z_0}\|} dz_0, \quad (1)$$

where, $Z \in \mathbb{N}$, $a \in \mathbb{R}^+$, $\vec{r} = (x, y, z)$ and $\vec{r}_{z_0} = (0, 0, z_0)$, (so that $\frac{\exp[-az_0^2]}{\|\vec{r} - \vec{r}_{z_0}\|} = \frac{\exp[-az_0^2]}{\sqrt{x^2 + y^2 + (z - z_0)^2}}$, or in cylindrical coordinates $\vec{r} = (\rho, \phi, z)$, $\frac{\exp[-az_0^2]}{\|\vec{r} - \vec{r}_{z_0}\|} = \frac{\exp[-az_0^2]}{\sqrt{\rho^2 + (z - z_0)^2}}$).

It corresponds to the Coulomb potential of an infinite wire with charge Z distributed according to a Gaussian function. In the limiting case of a Gaussian function sharply peaking at the origin ($a \rightarrow +\infty$, Dirac distribution limit), the system will tend toward a point-charge Z concentrated at the origin and the hydrogenoid atom eigenfunctions (‘‘Slater’’ orbitals) will be recovered.

However, by taking a Gaussian width parameter of the order of magnitude of a nucleus vibration amplitude, we will get basis functions corresponding to a Coulomb potential convoluted by a nuclear, vibrational, harmonic motion, that we may think particularly appropriate for

EN-MFCI calculations.

So, we consider the time-independent Schrödinger equation in axisymmetric coordinates

$$\left[\frac{-1}{2\mu} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \right) + V(\rho, z) - E \right] \psi(\rho, \phi, z) = 0, \quad (2)$$

defined on the Hilbert space of square integrable functions whose scalar product is expressed as,

$$\langle \psi_1 | \psi_2 \rangle := \int_0^{+\infty} \rho d\rho \int_0^{2\pi} d\phi \int_{-\infty}^{+\infty} dz \psi_1^*(\rho, \phi, z) \psi_2(\rho, \phi, z), \quad (3)$$

Setting,

$$\psi(\rho, \phi, z) = \exp(im\phi) f(\rho, z), \quad \text{for } m \in \mathbb{Z}, \quad (4)$$

the previous equation reduces to,

$$\left[\frac{-1}{2\mu} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial z^2} \right) + V(\rho, z) + \frac{m^2}{2\mu\rho^2} - E \right] f(\rho, z) = 0. \quad (5)$$

Restricting the search to bound states ψ , adds the normalization condition,

$$\int_0^{+\infty} \rho d\rho \int_{-\infty}^{+\infty} dz |f(\rho, z)|^2 = \frac{1}{2\pi}. \quad (6)$$

Then, setting,

$$f(\rho, z) = \frac{h(\rho, z)}{\sqrt{\rho}}, \quad (7)$$

the equation (5) further simplifies to,

$$\left[\frac{-1}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{\partial^2}{\partial z^2} \right) + V_{eff}(\rho, z) - E \right] h(\rho, z) = 0, \quad (8)$$

where,

$$V_{eff}(\rho, z) := V(\rho, z) + \frac{(m + \frac{1}{2})(m - \frac{1}{2})}{2\mu\rho^2}, \quad (9)$$

is an effective potential that includes a term of rotational origin. The normalization condition becomes,

$$\int_0^{+\infty} d\rho \int_{-\infty}^{+\infty} dz |h(\rho, z)|^2 = \frac{1}{2\pi}. \quad (10)$$

The effective potential has a singularity on the z -axis where the charge is spread out. The behaviour of $h(\rho, z)$ as ρ goes to zero can be derived from Eq.(8) by setting $h(\rho, z) \approx \rho^\beta g_0(z)$ (with $g_0(z)$ non identically zero on \mathbb{R}) and retaining only the dominant terms at this limit. We easily find $\beta = (m + \frac{1}{2})$. The condition (10) implies that $|h(\rho, z)|^2$ must be integrable at the limit $\rho \rightarrow 0$, hence $2\beta > -1$, and $m \geq 0$.

The same line of reasoning implies that, as ρ goes to infinity, the eigenfunction of a bound state must be exponentially damped by a factor $exp(-\sqrt{-2\mu E}\rho)$. This suggest a new change of variables, for negative values of E :

$$\sigma = \sqrt{-2\mu E}\rho, \quad (11)$$

$$y = \sqrt{-2\mu E}z, \quad (12)$$

and a formally simpler equation,

$$\left[\left(\frac{\partial^2}{\partial \sigma^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{V_{eff}(\sigma, y) - E}{E} \right] h(\sigma, y) = 0. \quad (13)$$

The solution can be tentatively searched in the form of a series,

$$h(\sigma, y) = exp(-\sigma - y)\sigma^{m+\frac{1}{2}} \sum_{i=0}^{+\infty} g_i(y)\sigma^i. \quad (14)$$

On another hand, the potential $V(\rho, z)$ can be transformed into a series according to

$$\begin{aligned}
V(\rho, z) &= \frac{-Z\sqrt{a}}{\pi} \int_0^{+\infty} \frac{d\lambda}{\sqrt{\lambda}} \int_{-\infty}^{+\infty} dz_0 \exp[-az_0^2 - \lambda(\rho^2 + (z - z_0)^2)] \\
&= -Z\sqrt{\frac{a}{\pi}} \int_0^{+\infty} \frac{d\lambda}{\sqrt{\lambda(a+\lambda)}} \exp[-\lambda\rho^2] \exp[-\frac{a\lambda}{a+\lambda}z^2] \\
&= -Z\sqrt{\frac{a}{\pi}} \sum_{j=0}^{+\infty} \frac{(-az^2)^j}{j!} \Gamma[j + \frac{1}{2}] U[j + \frac{1}{2}, 1, a\rho^2] \\
&= -Za \sum_{j=0}^{+\infty} \frac{\Gamma[j+\frac{1}{2}]}{\Gamma[\frac{1}{2}]\Gamma[j+1]} U[j + \frac{1}{2}, 1, a\rho^2] (-az^2)^j, \tag{15}
\end{aligned}$$

where $U[a, b, x] := \int_0^{+\infty} d\nu \exp[-\nu x] \nu^{a-1} (1+\nu)^{b-a-1}$ is the hypergeometric ‘‘U’’ function, and $\Gamma[x]$ the gamma function.

References

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