50th Karpacz Winter School of Theoretical Physics

H_2 molecule as a two-site system with the *ab initio* optimization of single-particle wave functions in the correlated state revisited: Electron–proton coupling

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FNP Foundation for Polish Science
INNOVATIVE ECONOMY NATIONAL COHESION STRATEGY
EUROPEAN UNION EUROPEAN REGIONAL DEVELOPMENT FUND

Motivation

We want to have a realistic model of the H_2 molecule. We start from Hamiltonian (frame *Hamiltonian*) with all one- and two-body interactions.

The main aims are to:

1. solve exactly the two-site Hamiltonian (frame *Solution*),
2. calculate the expressions for the microscopic parameters from the first principles (frame *Microscopic Parameters*),
3. optimize the single-particle wave-function to minimize the energy,
4. calculate the electron–ion couplings (frame *Electron–proton coupling*),
5. evaluate the zero-point motion (frame *Results*).

Hamiltonian

$$\begin{aligned}\mathcal{H} =&\epsilon\left(\hat{n}_1+\hat{n}_2\right)+t\sum_{\sigma}\left(\hat{a}^{\dagger}_{1\sigma}\hat{a}_{2\sigma}+\hat{a}^{\dagger}_{2\sigma}\hat{a}_{1\sigma}\right)\\&+U\left(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow}+\hat{n}_{2\uparrow}\hat{n}_{2\downarrow}\right)-2J\mathbf{S}_1\mathbf{S}_2\\&+\left(K-\frac{J}{2}\right)\hat{n}_1\hat{n}_2+J\left(\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{1\downarrow}\hat{a}_{2\downarrow}\hat{a}_{2\uparrow}+h.c.\right)\\&+V\sum_{\sigma}\left[\left(\hat{n}_{1\sigma}+\hat{n}_{2\sigma}\right)\left(\hat{a}^{\dagger}_{1\bar{\sigma}}\hat{a}_{2\bar{\sigma}}+\hat{a}^{\dagger}_{2\bar{\sigma}}\hat{a}_{1\bar{\sigma}}\right)\right],\end{aligned}$$

ϵ is a single-particle energy, t the hopping parameter, U the on-site Coulomb repulsion, K the inter-site Coulomb repulsion, J the exchange integral and V the so-called correlated hopping.

We also use implicit form $\mathcal{H}=\sum_i \Xi_i\hat{O}_i$, where Ξ_i is symbolic notation of any of the microscopic parameters and $\hat{O}_i$ the notation of the respective operator.

Parameters evaluation

We choose the Slater $1s$ basis

$$\Psi_i\left(\mathbf{r}\right)=\sqrt{\frac{\alpha^3}{\pi}}e^{-\alpha|\mathbf{r}-\mathbf{R_i}|},$$

where α is the inverse size of the orbital. To ensure orthogonality we use Wannier functions which in this case reduce the superposition of the atomic states, i.e.,

$$w_i\left(\mathbf{r}\right)=\beta\Big(\Psi_i\left(\mathbf{r}\right)-\gamma\Psi_j\left(\mathbf{r}\right)\Big),$$

with the mixing parameters $\beta=\frac{1}{\sqrt{2}}\sqrt{\frac{1+\sqrt{1-S^2}}{1-S^2}}$ and $\gamma=\frac{S}{1+\sqrt{1-S^2}}$, where $S=S(\alpha,R)\equiv\langle\Psi_1|\,\Psi_2\rangle$ is the atomic functions' overlap.

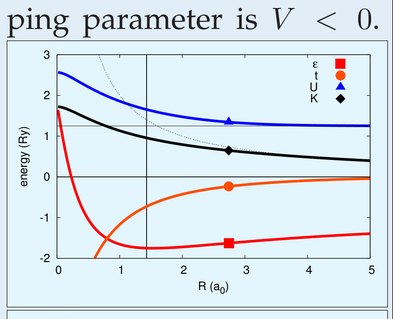
Microscopic Parameters

The microscopic parameters $\epsilon=T_{11}$, $t=T_{12}$, $U=V_{1111}$, $J=V_{1212}$, $K=V_{1122}$ and $V=V_{1112}$ correspond to one– and two-particle interactions

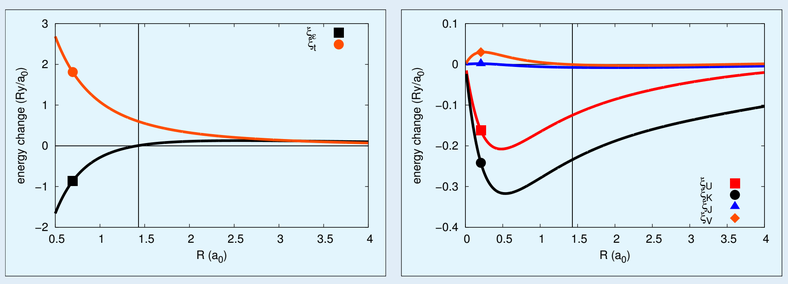
$$\begin{aligned}T_{ij}&=\langle w_i|\,\mathcal{T}\,|w_j\rangle,\\V_{ijkl}&=\langle w_iw_j|\,\mathcal{V}_{12}\,|w_kw_l\rangle,\end{aligned}$$

where in atomic units $\mathcal{T}=-\bigtriangledown^2-2/|\mathbf{r}-\mathbf{R}|$, and $\mathcal{V}=2/|\mathbf{r}-\mathbf{r}'|$.

Figs: Microscopic parameters ϵ, t, U, K, J and V versus average interionic distance R. Note the convergence of the intersite Coulomb repulsion K to the classical value $2/R$ (dashed line) at $R\to\infty$. The on-site repulsion U reaches also its atomic limit $U_{at}=1.25\ Ry$, whereas the hopping parameter $t\to 0$. The exchange integral is always ferromagnetic, and the so-called correlated hopping parameter is $V<0$.



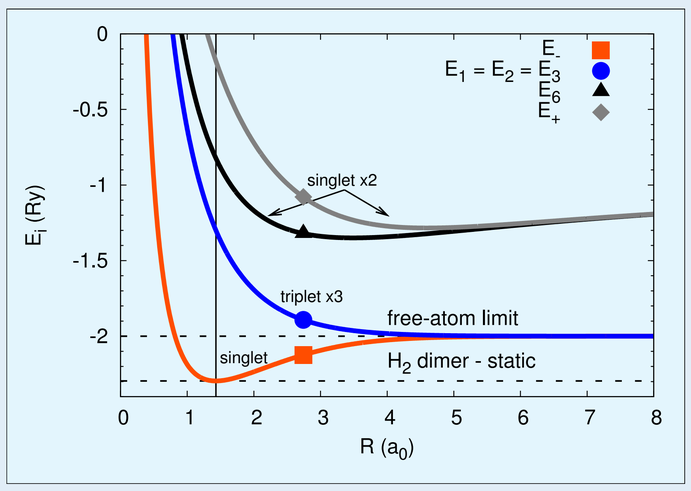
Electron–proton coupling



Figs: Coupling constants ξ_ϵ, ξ_t, ξ_U, ξ_K, ξ_J and ξ_V versus intersite distance R.

Solution

Solutions of our electronic Hamiltonian are listed in the table below. For given interionic distance R, our procedure requires us to minimize the energy $E_i=E_i^e+\frac{2}{R}$ with respect to α.



i	Eigenvector $\lvert i\rangle$	Eigenenergy E_i^e
1	$\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\uparrow}\lvert 0\rangle$	$2\epsilon+K-J$
2	$\hat{a}^{\dagger}_{1\downarrow}\hat{a}^{\dagger}_{2\downarrow}\lvert 0\rangle$	$2\epsilon+K-J$
3	$\frac{1}{\sqrt{2}}\left(\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\downarrow}+\hat{a}^{\dagger}_{1\downarrow}\hat{a}^{\dagger}_{2\uparrow}\right)\lvert 0\rangle$	$2\epsilon+K-J$
6	$\frac{1}{\sqrt{2}}\left(\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{1\downarrow}-\hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{2\downarrow}\right)\lvert 0\rangle$	$2\epsilon+U-J$
$+$	$\frac{(K-U-\mathcal{D})\lvert 4\rangle+4\lvert t+V\rvert\rvert 5\rangle}{\sqrt{2\mathcal{D}(\mathcal{D}-U+K)}}$	$2\epsilon+\frac{U+K}{2}+J+\frac{1}{2}\mathcal{D}$
$-$	$\frac{(U-K+\mathcal{D})\lvert 4\rangle+4\lvert t+V\rvert\rvert 5\rangle}{\sqrt{2\mathcal{D}(\mathcal{D}+U-K)}}$	$2\epsilon+\frac{U+K}{2}+J-\frac{1}{2}\mathcal{D}$

$\mathcal{D}=\sqrt{(U-K)^2+16\left(t+V\right)^2}$, $|4\rangle=\sqrt{2}^{-1}\left(\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\downarrow}-\hat{a}^{\dagger}_{1\downarrow}\hat{a}^{\dagger}_{2\uparrow}\right)|0\rangle$, and $|5\rangle=\sqrt{2}^{-1}\left(\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{1\downarrow}+\hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{2\downarrow}\right)|0\rangle$.

Fig: The energy E_i versus intersite distance R. Clearly, the spin-singlet state $|-\rangle$ is the equilibrium state.

Evaluation of the zero-point motion

We introduce the zero-point motion by extending the Hamiltonian in terms of displacement δR

$$\mathcal{H}\to\mathcal{H}_{\delta R}=\mathcal{H}+\delta\mathcal{H}+\mathcal{H}_{ZPM},$$

where

$$\langle\delta\mathcal{H}\rangle=\sum_i\xi_i\delta R\left\langle\hat{O}_i\right\rangle-\frac{2}{R_B^2}\delta R,$$

where $\xi_i=\delta\Xi_i/\delta R$ are the coupling coefficients (see frame *Electron–proton coupling*).

$$\langle\mathcal{H}_{ZPM}\rangle=2\frac{\delta p^2}{2M_{H^-}}+\sum_{i=2}^{9}\frac{1}{i!}E_B^{(i)}\delta R^i+o\left(\delta R^{10}\right),$$

where δp is the momentum of the H^- ion with mass M_{H^-}.

We evaluate the value of δp from the Heisenberg principle and we minimize $\langle\mathcal{H}_{\delta R}\rangle$ with respect to δR.

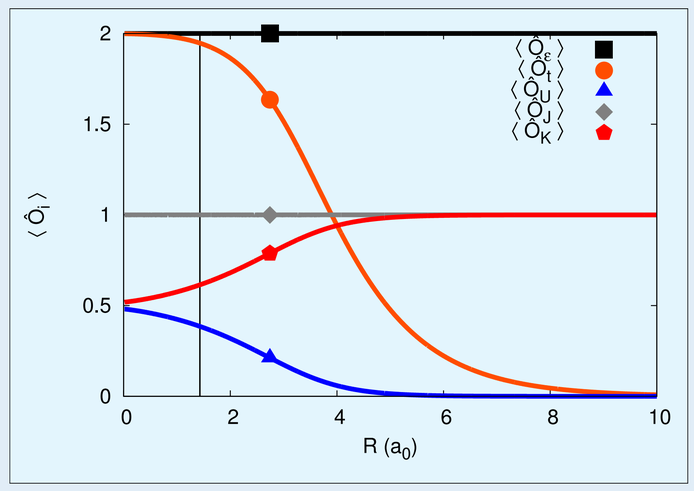


Fig: Averages of the operator part in Hamiltonian, calculated in the ground-state versus distance R. They are of the order of unity.

Results

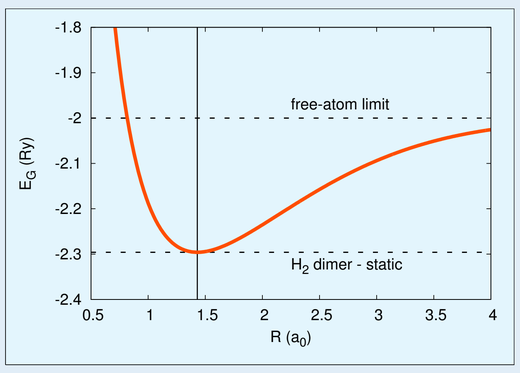


Fig: The equilibrium energy versus distance R.

We find the binding energy and distance

$$R_B=1.43017\ a_0,$$

$$E_B=-2.29587\ Ry.$$

We also evaluate the zero-point motion amplitude

$$|\delta\mathbf{R}|=0.189028\ a_0$$

and energy

$$E_{ZPM}=0.024072Ry,\quad\Delta E_{ZPM}=\frac{|E_{ZPM}|}{|E_B|}=1.0485\%.$$

Acknowledgments

The work was realised in the Project TEAM awarded to our group by the Foundation for Polish Science (FNP) for the years 2011-2014. The partial support by the special Grant MAESTRO, No. DEC-2012/04/A/ST3/00342, from the National Science Center (NCN) for the years 2012-2017 should also be acknowledged. APK visit at the University of Parma has been supported by the grant of the Polish Ministry of Science and Higher Education, Grant No. 7150/E-338/M/2013.

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