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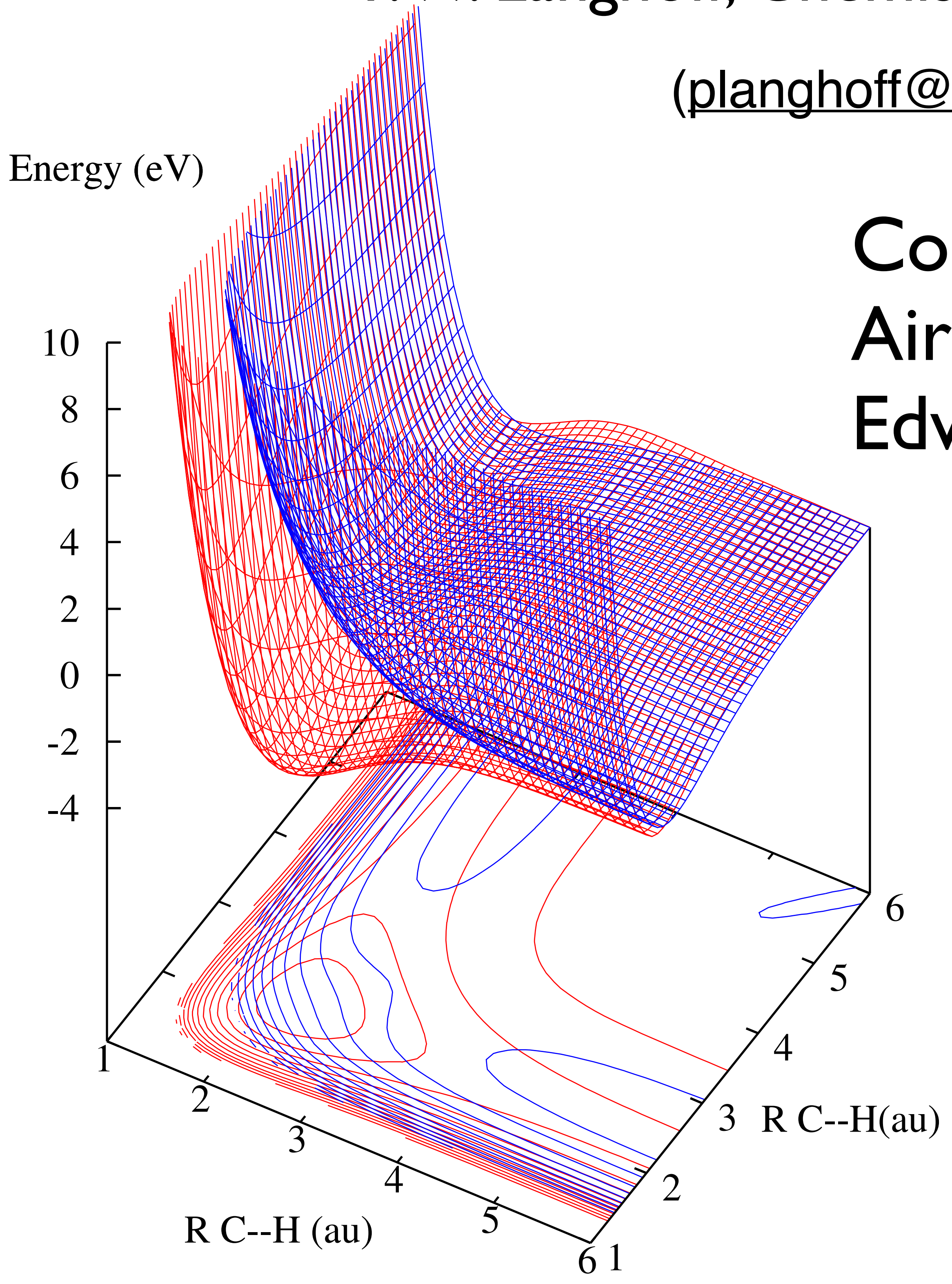
The Atom in a Molecule: Implications for Molecular Structures and Properties

P.W. Langhoff, Chemistry & Biochemistry, UCSD

(planghoff@mail.ucsd.edu)



Co-Workers: J.D. Mills, J.A. Boatz
Air Force Research Laboratory
Edwards AFB, CA

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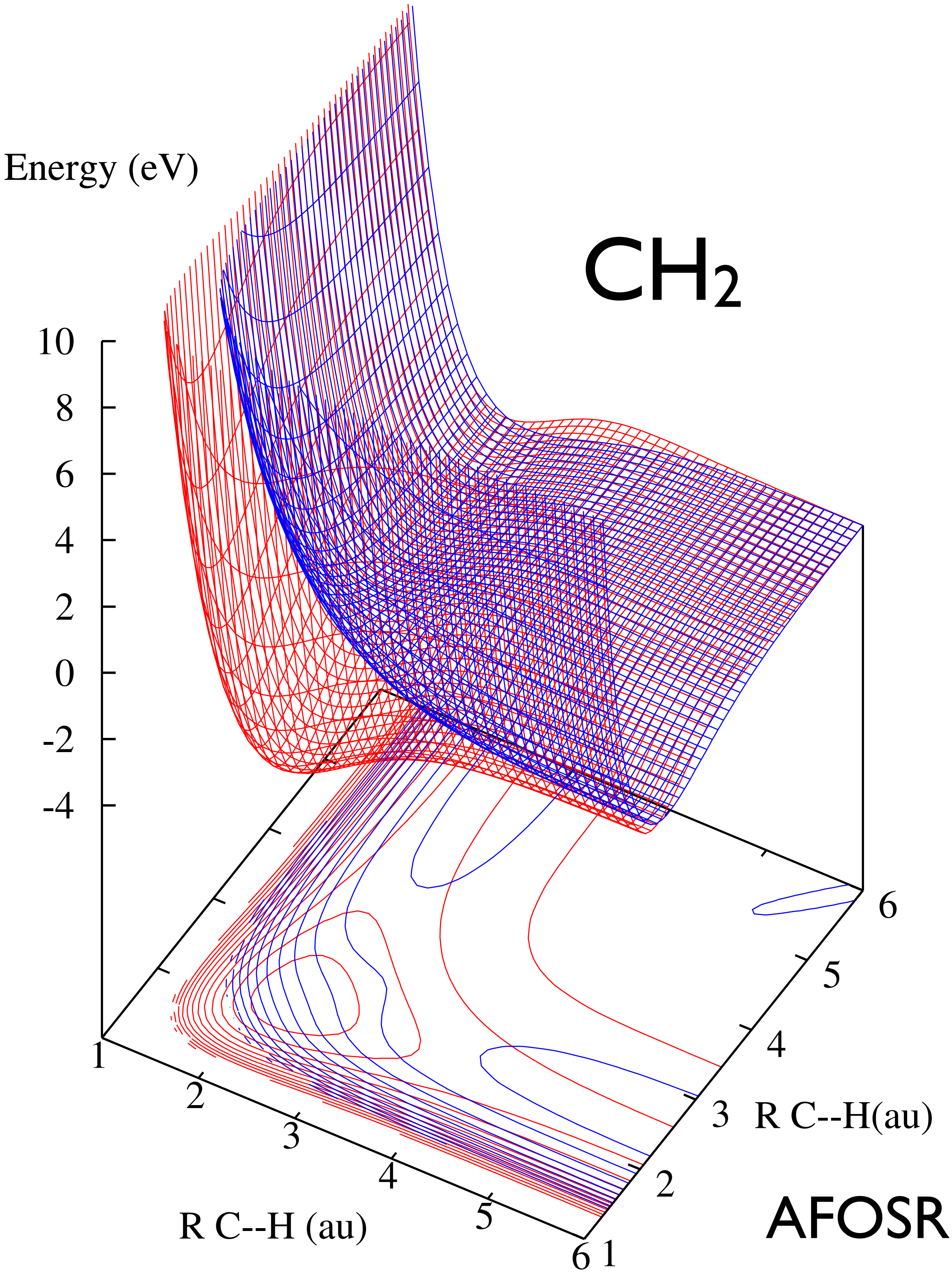
Exact Atomic-Pair Theory of Molecular Hamiltonians



J.D. Mills, J.A. Boatz - AFRL
J.A. Sheehy - NASA
R.J. Hinde - UT, Knoxville
S. Elbert - PNNL
C. L. Winstead - Cal Tech
M. Ben-Nun, K. Rollin - UCSD
M. Bromley - SDSU
J. Lee - Accelrys
G.A. Gallup - UN, Lincoln
J.F. Rico, R. Lopez - UA, Madrid
J.A. McCammon Group - UCSD

AFOSR, AFRL, NAS-NRC, EOARD, ASEE, NSF, NIH

“… all things are made of atoms…” R.P. Feynman - 1963

When atoms come together their orbitals are distorted significantly…

Electronic charge is transferred among the atoms present…

Even inner atomic orbitals are affected by molecular formation…

As a consequence, one way or another, “chemical bonds” are formed…

Can we perform calculations to make these familiar qualitative atomic distortion and chemical bonding notions quantitative…

“…since there is no specific assignment of the electrons occurring in the system to the nuclei involved, hence there are no atoms, isomers, conformations, etc…” - P.-O. Löwdin - 1988

“A quantum system always has a Hamiltonian,…” P.A.M. Dirac - 1930

What is the Hamiltonian operator for an atom in a molecule?

Molecular Hamiltonian Operators

$$\hat{H}^{(\alpha)}(\boldsymbol{i}) = \sum_{i}^{n_\alpha} \Big\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i'=i+1}^{n_\alpha} \frac{e^2}{r_{ii'}} \Big\}$$

$$\hat{H}(\boldsymbol{r} : \boldsymbol{R}) = \sum_{\alpha=1}^{N} \hat{H}^{(\alpha)}(\boldsymbol{i}) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \hat{V}^{(\alpha,\beta)}(\boldsymbol{i}; \boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})$$

$$\hat{V}^{(\alpha,\beta)}(\boldsymbol{i}; \boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) = \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_{i}^{n_\alpha} \frac{Z_\beta e^2}{r_{i\beta}} - \sum_{j}^{n_\beta} \frac{Z_\alpha e^2}{r_{j\alpha}} + \sum_{i}^{n_\alpha} \sum_{j}^{n_\beta} \frac{e^2}{r_{ij}}$$

Fragment operators are not invariant to electron permutations.

If electron 1 and 7, say, are interchanged, the operators change.

Fragment operators do not commute with electron exchange.

Their expectation values with antisymmetric functions are ill defined.

Atomic-Product Representations of Molecules

Following Eisenschitz and London, Z. Physik, 60, 491 (1930):

Employ “van der Waals” products of atomic states to represent molecules:

$$\Phi(r:R) = \left\{\Phi^{(1)}(1) \otimes \Phi^{(2)}(2) \otimes \cdots \Phi^{(N)}(n)\right\}_O$$

P.W. Langhoff, J. Phys. Chem. **100**, 2974 (1996) - Karplus Festschrift

In this representation the electrons “stay home” with each nucleus.

Atomic fragment operators are well-defined over product representations.

Expectation values of fragment operators are similarly well-defined.

So-called non-Pauli states must be eliminated from the development!

Hamiltonian Matrix in the Atomic-Product Basis

$$\boldsymbol{H}(\boldsymbol{R}) \equiv \langle \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}(\boldsymbol{r}:\boldsymbol{R})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle$$

$$= \sum_{\alpha=1}^{N} \boldsymbol{H}^{(\alpha)} + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$$

One-atom matrix elements:

$$\boldsymbol{H}^{(\alpha)} = \langle \boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i}:\boldsymbol{R}_\alpha)|\hat{H}^{(\alpha)}(\boldsymbol{i})|\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i}:\boldsymbol{R}_\alpha)\rangle \equiv \boldsymbol{E}^{(\alpha)}$$

Two-atom matrix elements:

$$\boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \langle \boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\hat{V}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})\rangle$$

Technical Questions Addressed: J. Chem. Phys. **121**, 9323 (2004),

Theor. Chem. Acc. **120,**194 (2008), J. Phys. Chem. **113** 7687 (2009)

Universal Molecular Energy Expression

$$\Psi(r:R) \equiv \Phi(r:R) \cdot U_H(R)$$

$$E(R) \equiv {U_H}^{\dagger}(R) \cdot H(R) \cdot U_H(R)$$

$$= \sum_{\alpha=1}^{N} E^{(\alpha)}(R) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} V^{(\alpha,\beta)}(R)$$

Atomic energy matrices:

$$E^{(\alpha)}(R) \equiv {U_H}^{\dagger}(R) \cdot H^{(\alpha)} \cdot U_H(R)$$

Interaction energy matrices:

$$V^{(\alpha,\beta)}(R) \equiv {U_H}^{\dagger}(R) \cdot V^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot U_H(R)$$

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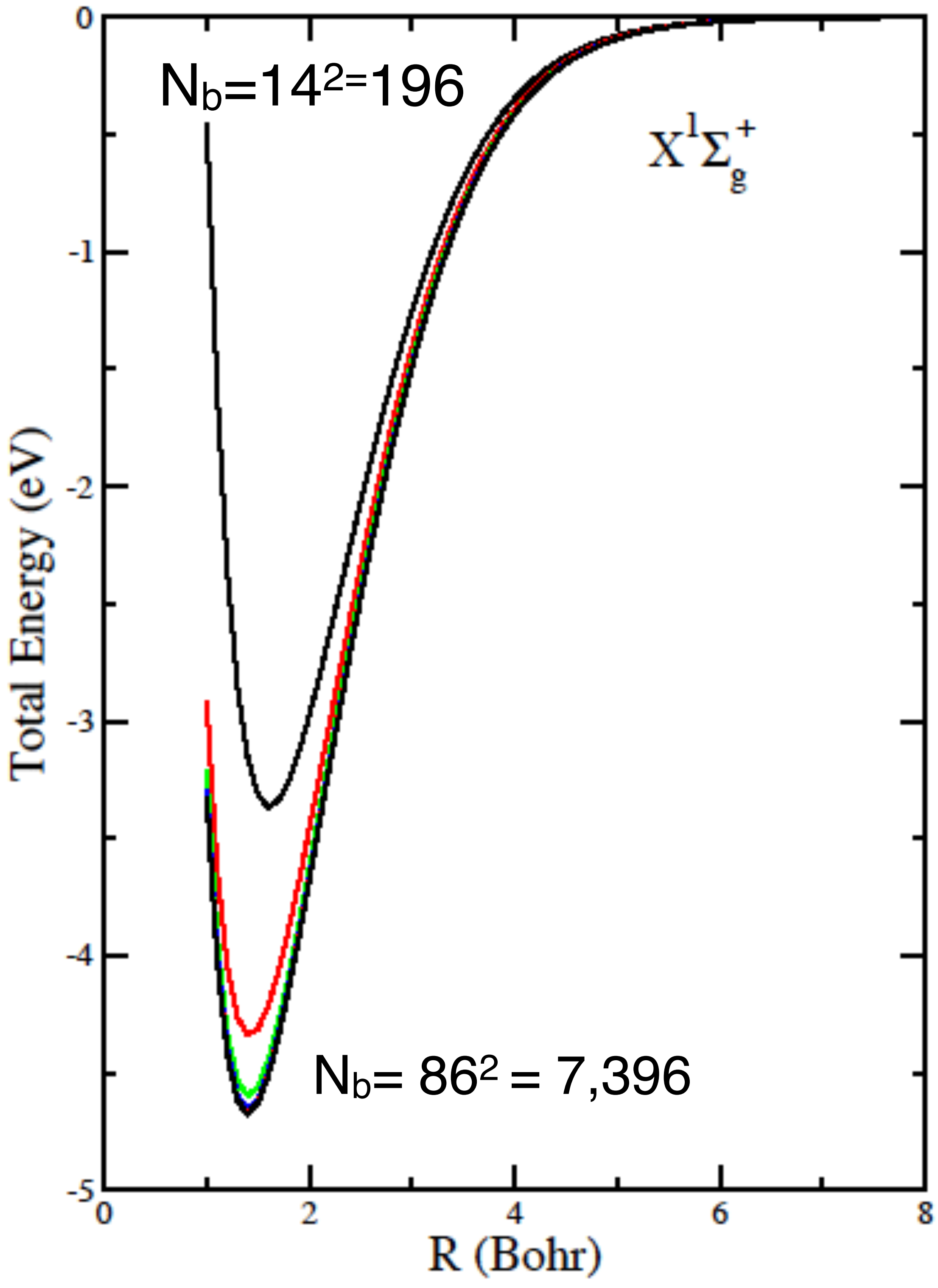
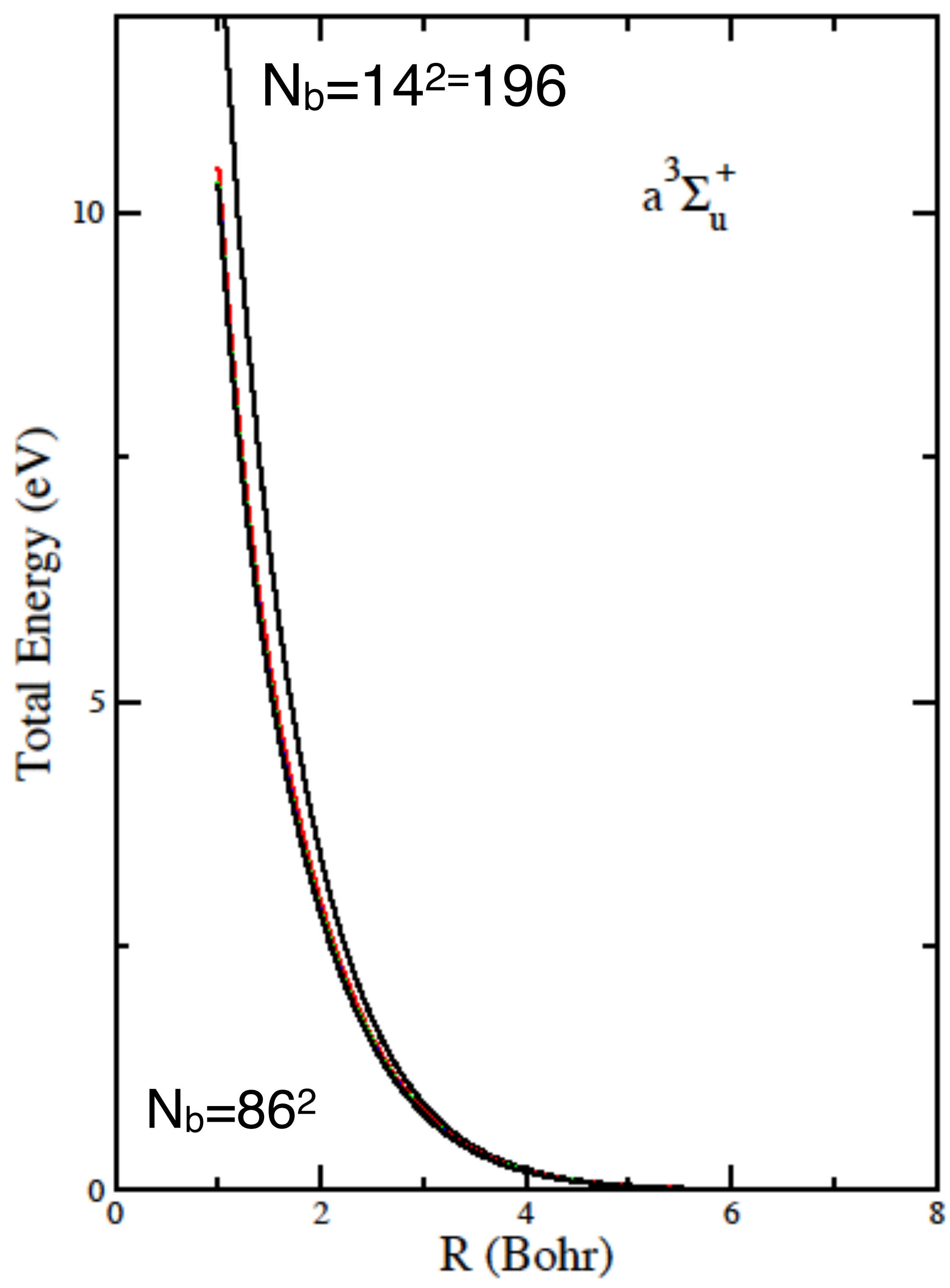
H_2 Electronic Energy Curves

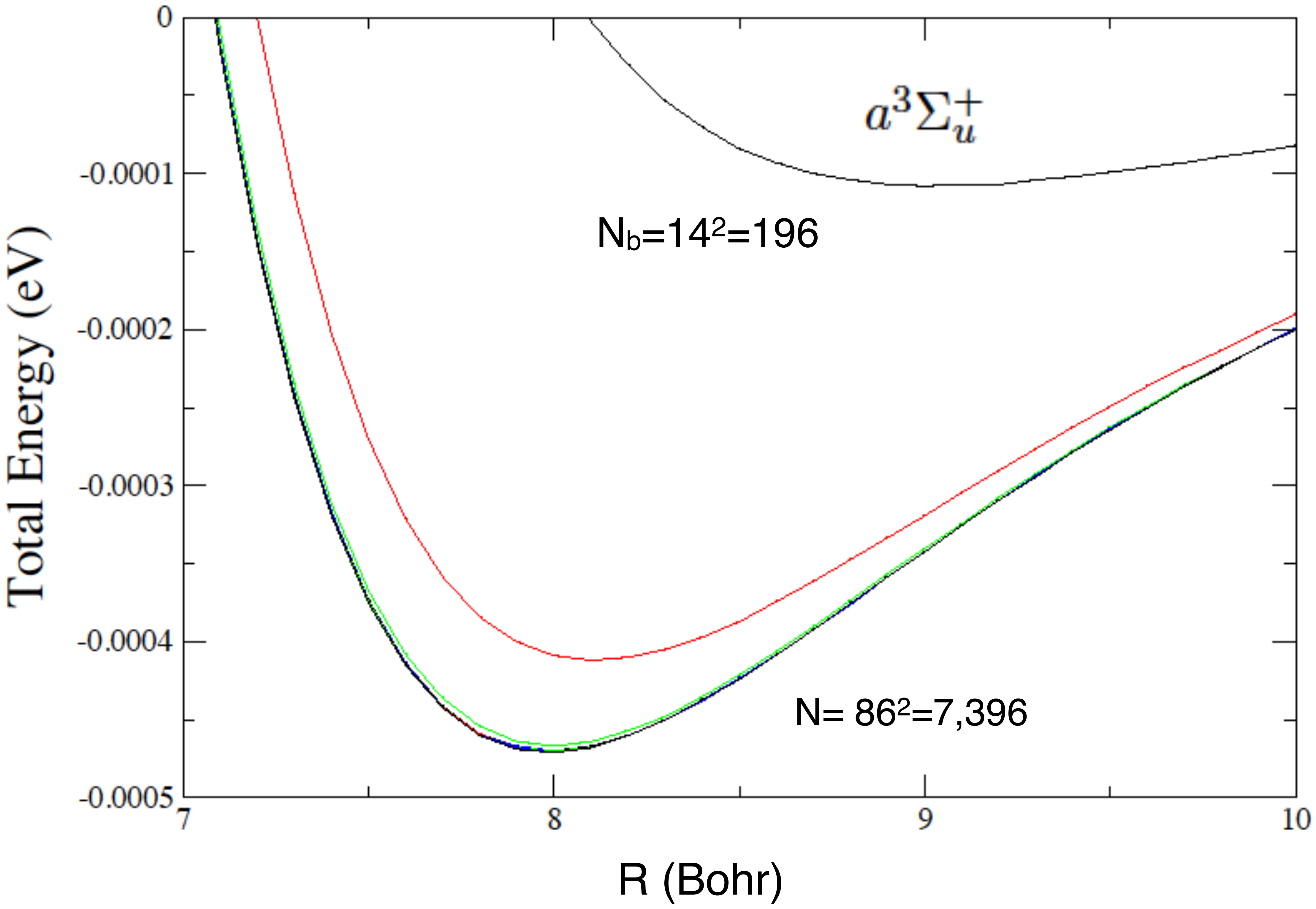


(a) Calculauted total electronic energy curve for the $X^1\Sigma_g^+$ state in molecular hydrogen - H_2.



(b) Calculated total electronic energy curve for the $a^3\Sigma_u^+$ state in molecular hydrogen - H_2.

van der Waals Interaction in Triplet H_2



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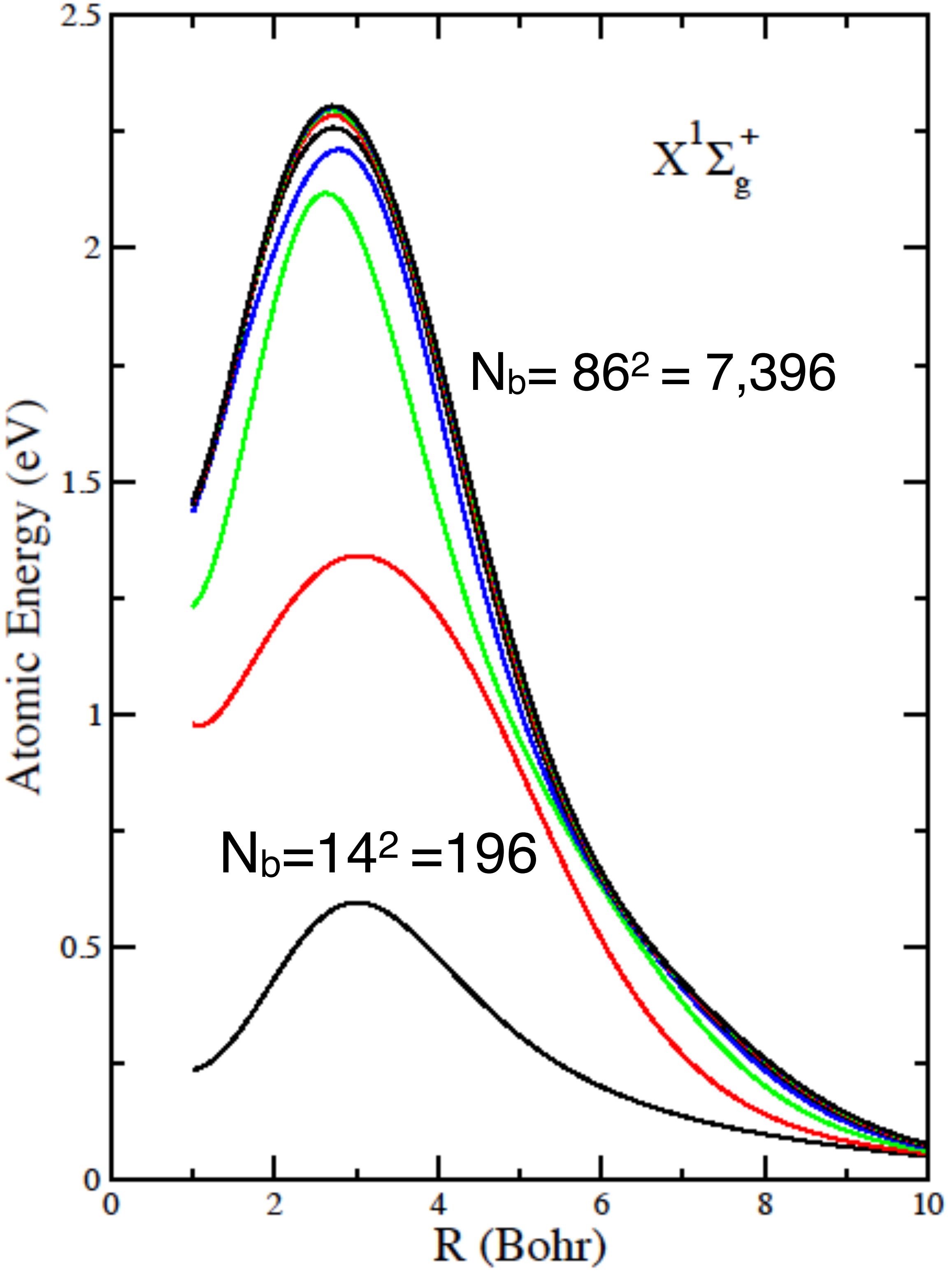
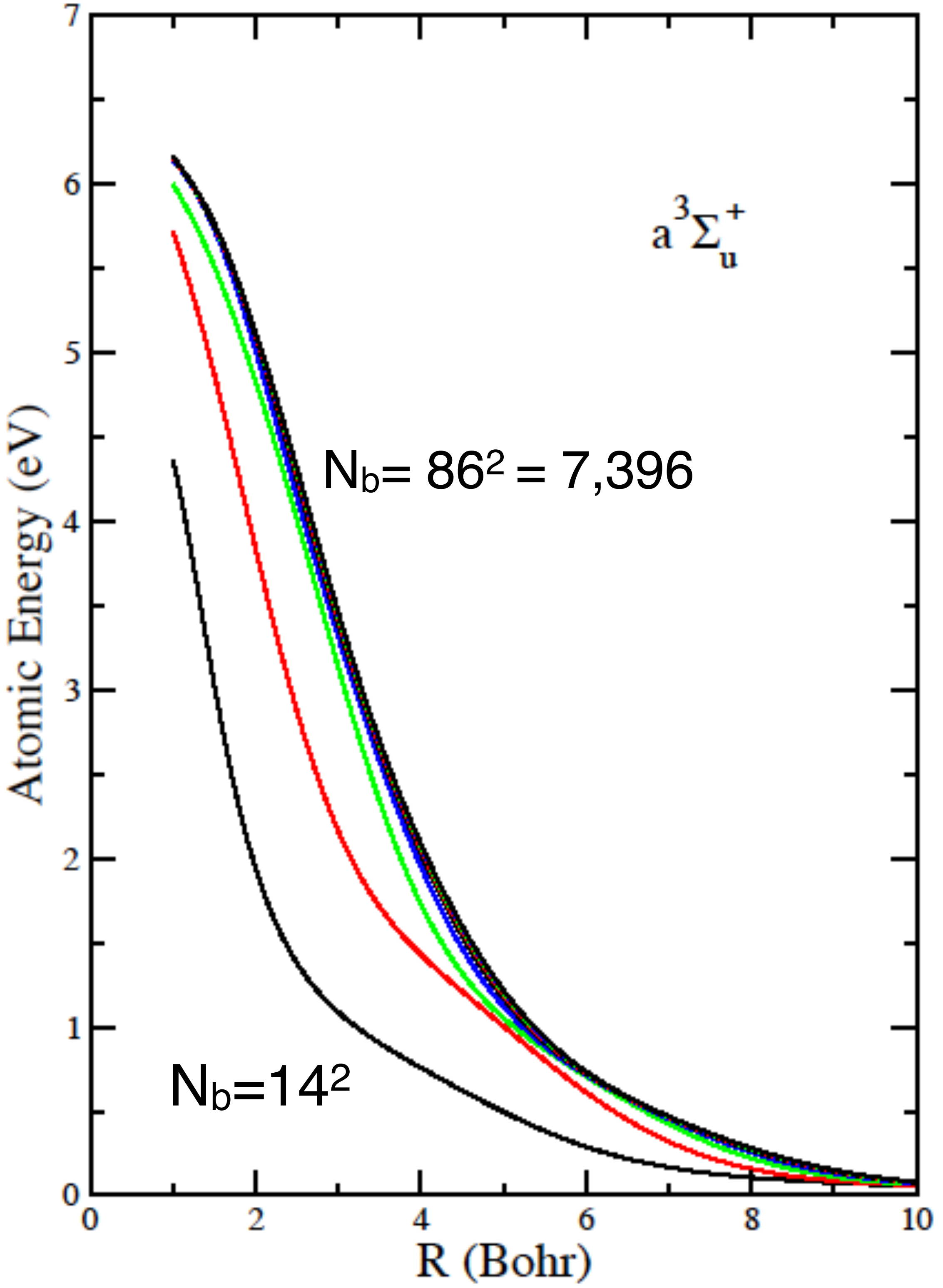
Atomic Promotion Energies in H_2

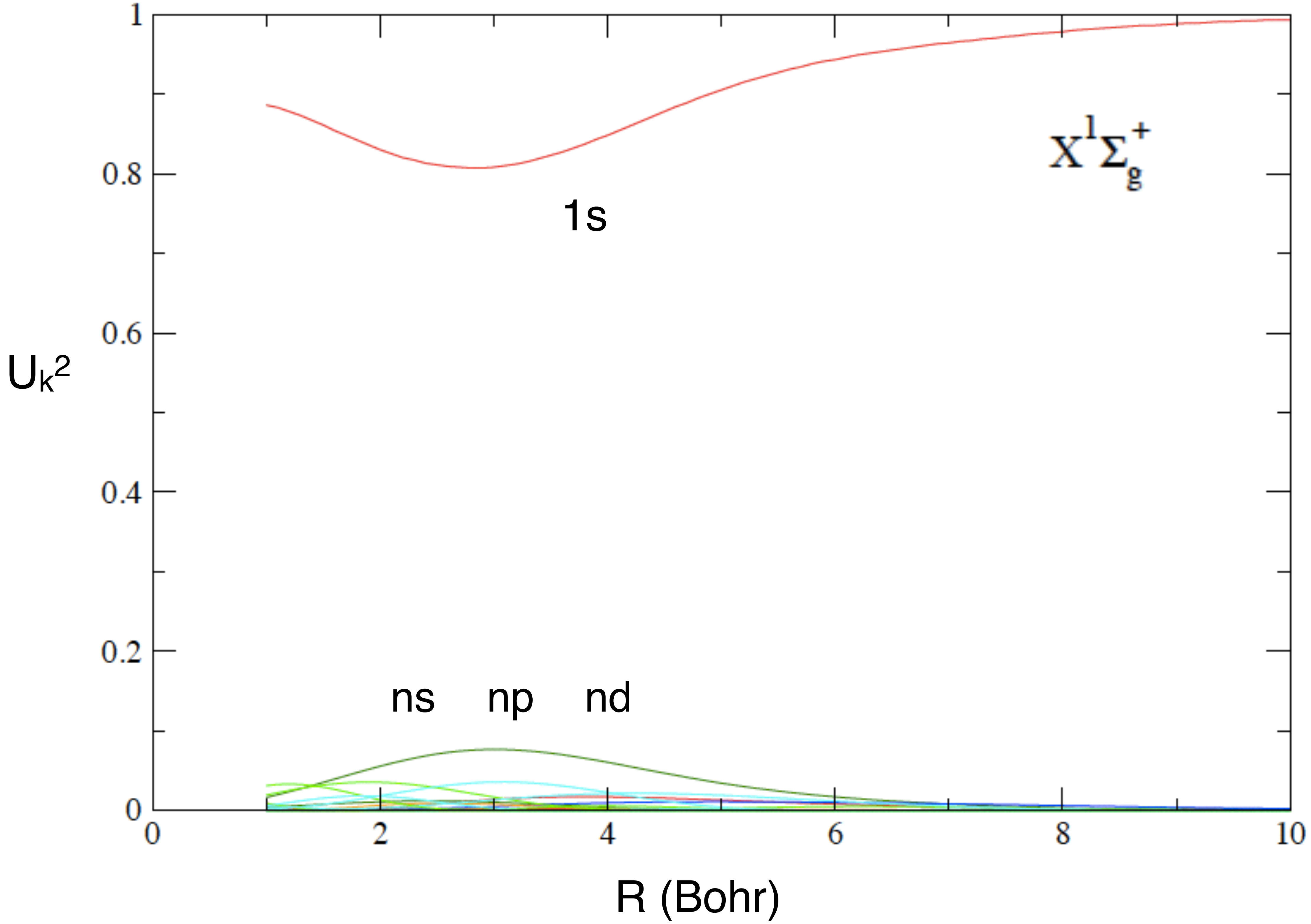


(a) Calculated individual hydrogen atom promotion energy curve in the $X^1\Sigma_g^+$ state of molecular hydrogen - H_2.

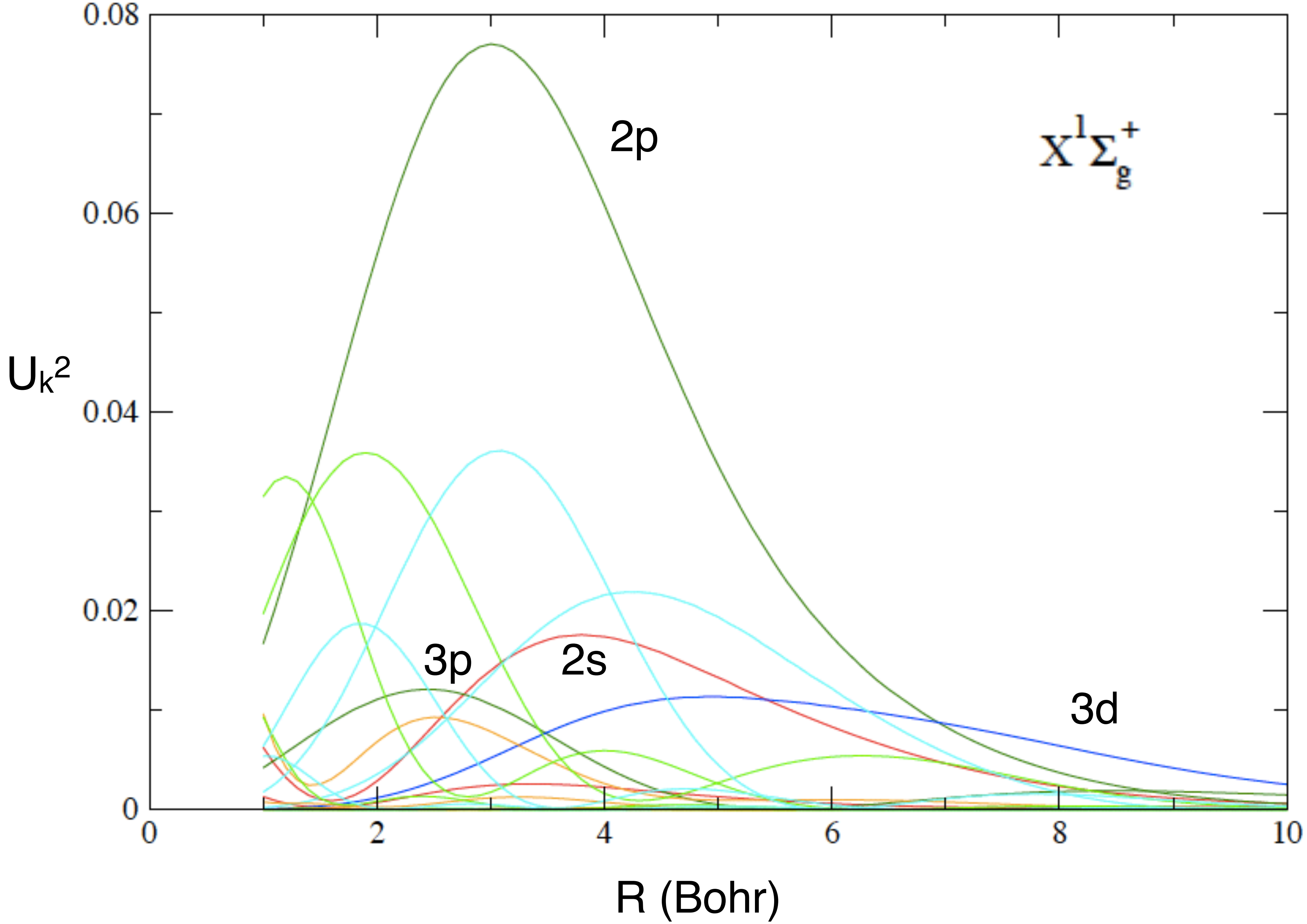


(b) Calculated individual hydrogen atom promotion energy curve in the $a^3\Sigma_u^+$ state of molecular hydrogen - H_2.

Atomic State Distribution in H_2



Atomic State Distribution in H_2



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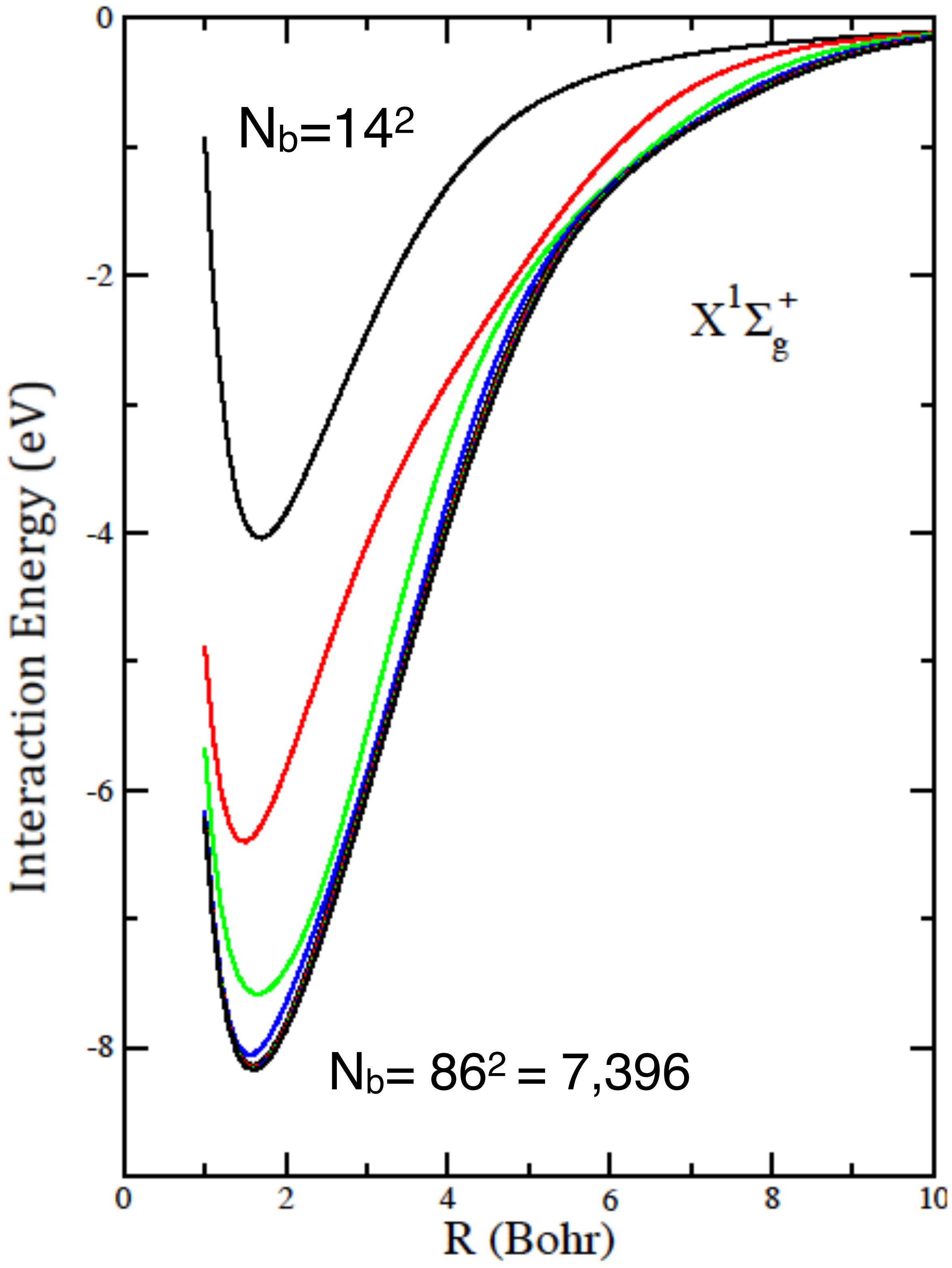
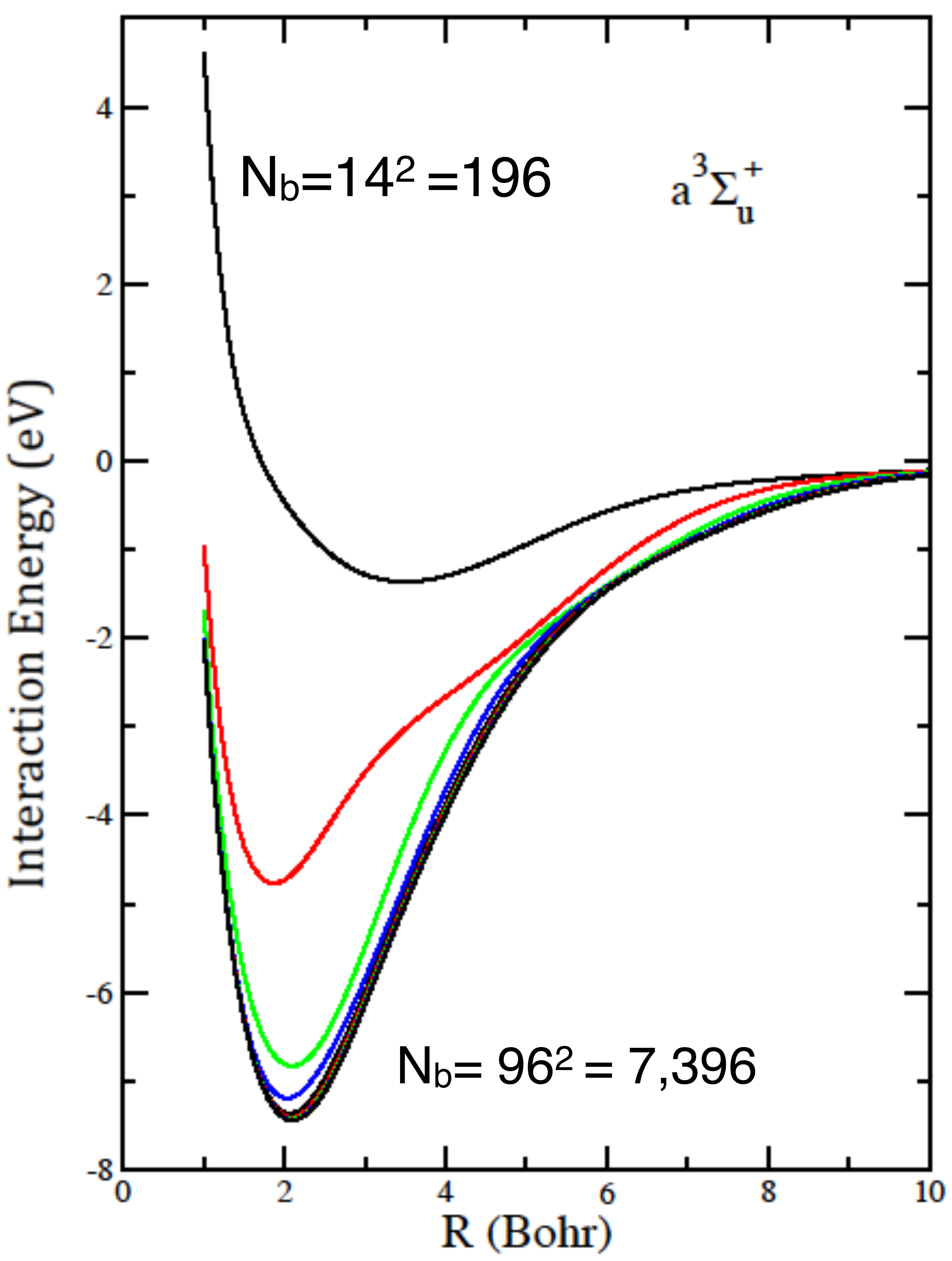
Atomic Interaction Energies in H_2

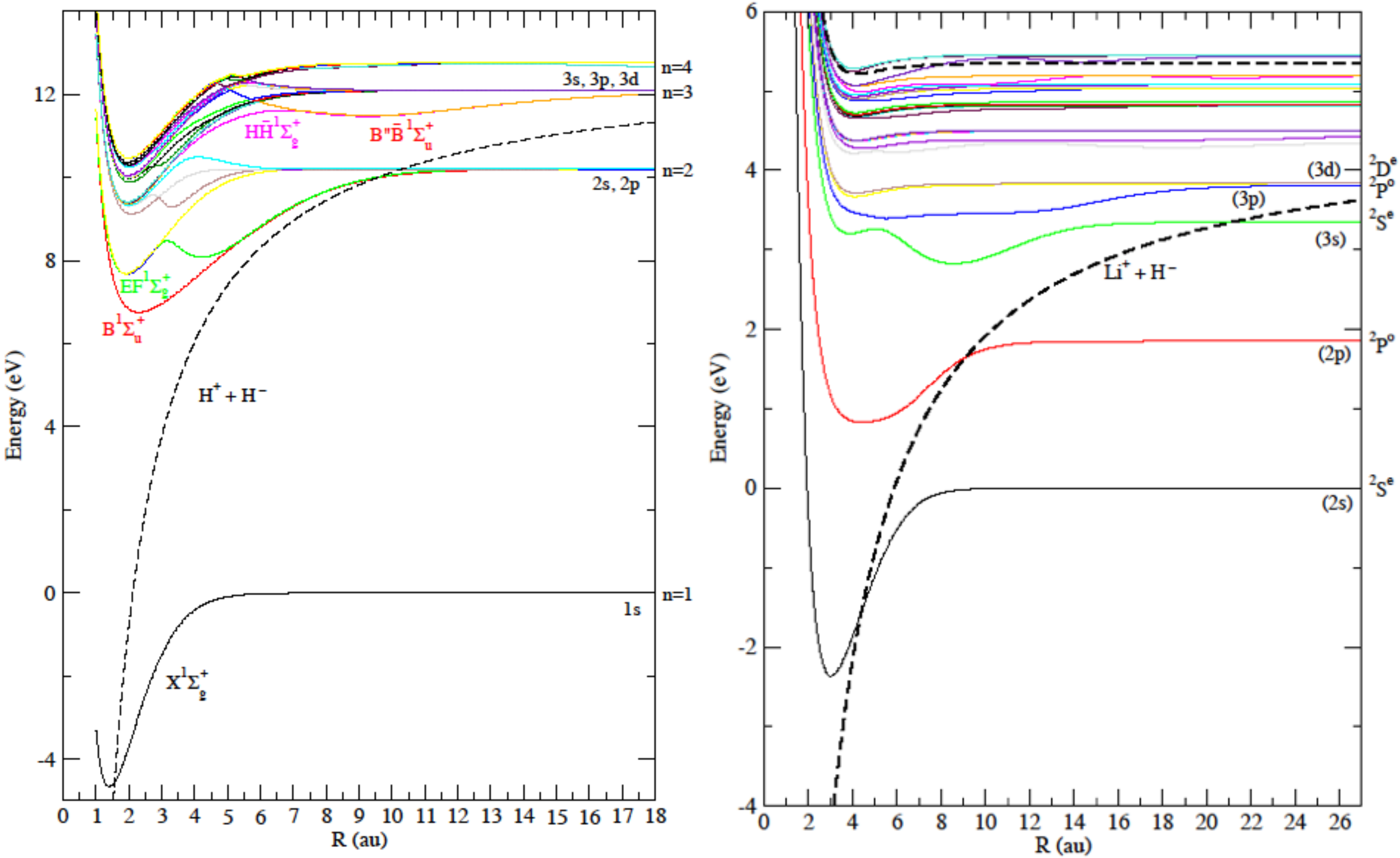


(a) Chemical intraction energy between hydroger atoms in the $X^1\Sigma_g^+$ state of molecular hydrogen - H_2.



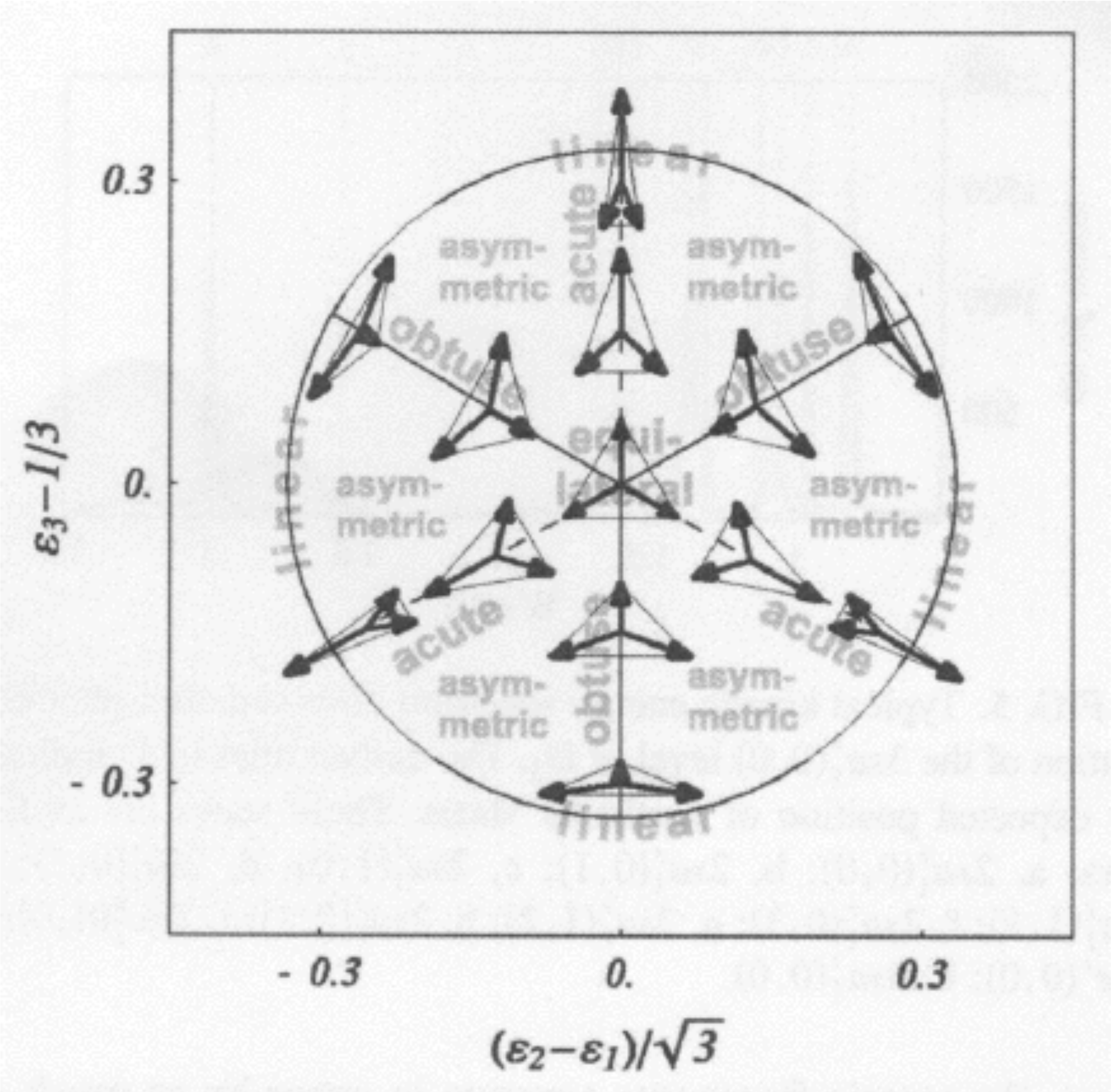
(b) Chemical interaction energy between hydrogen atoms in the $a^3\Sigma_u^+$ state of molecular hydrogen - H_2.

Charge Transfer in van der Waals Representations



Calculations of excited states in H_2 and LiH employing van der Waals representations

Photodissociation Pathways to Atomic Entanglements in H_3



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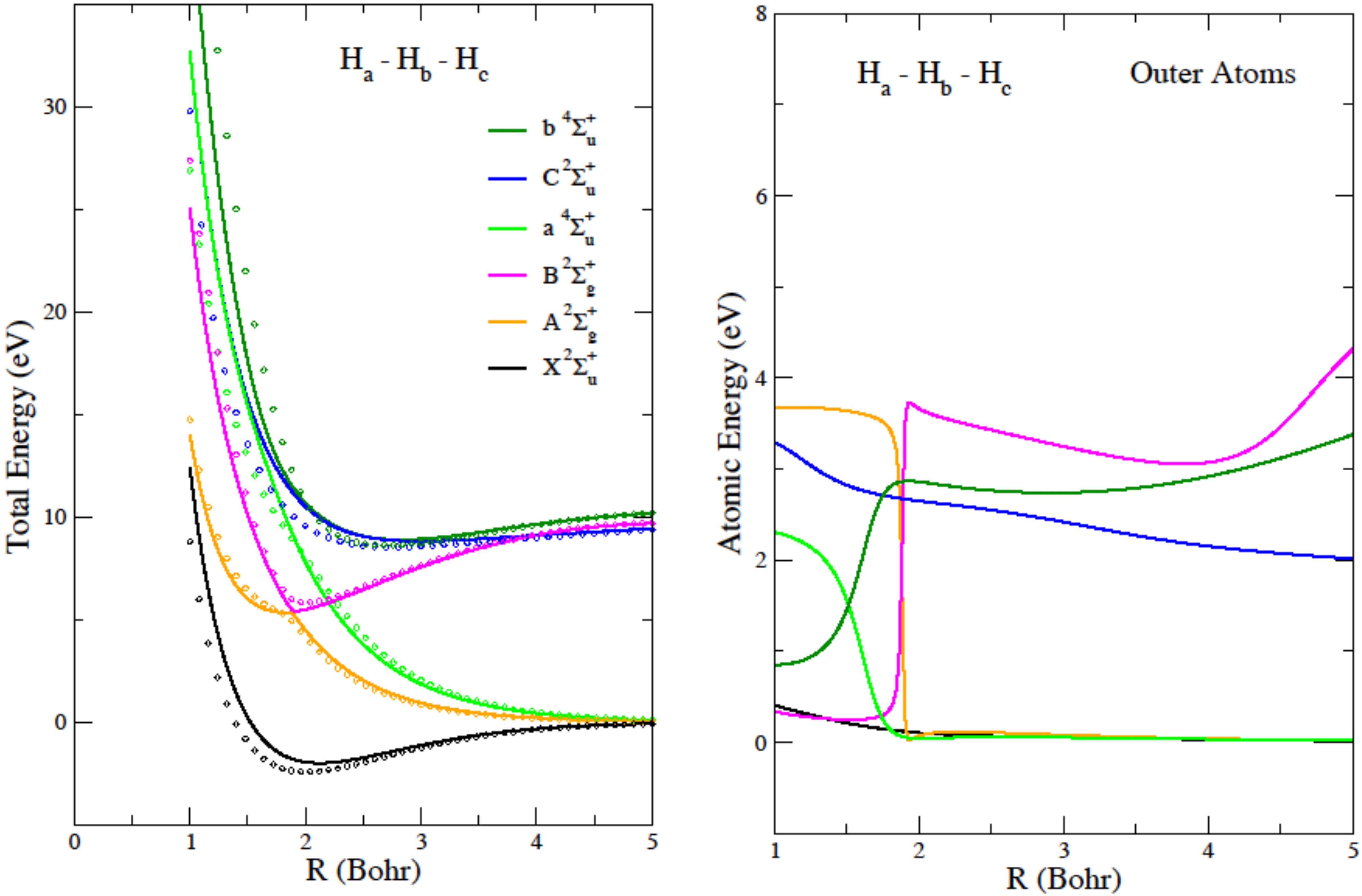
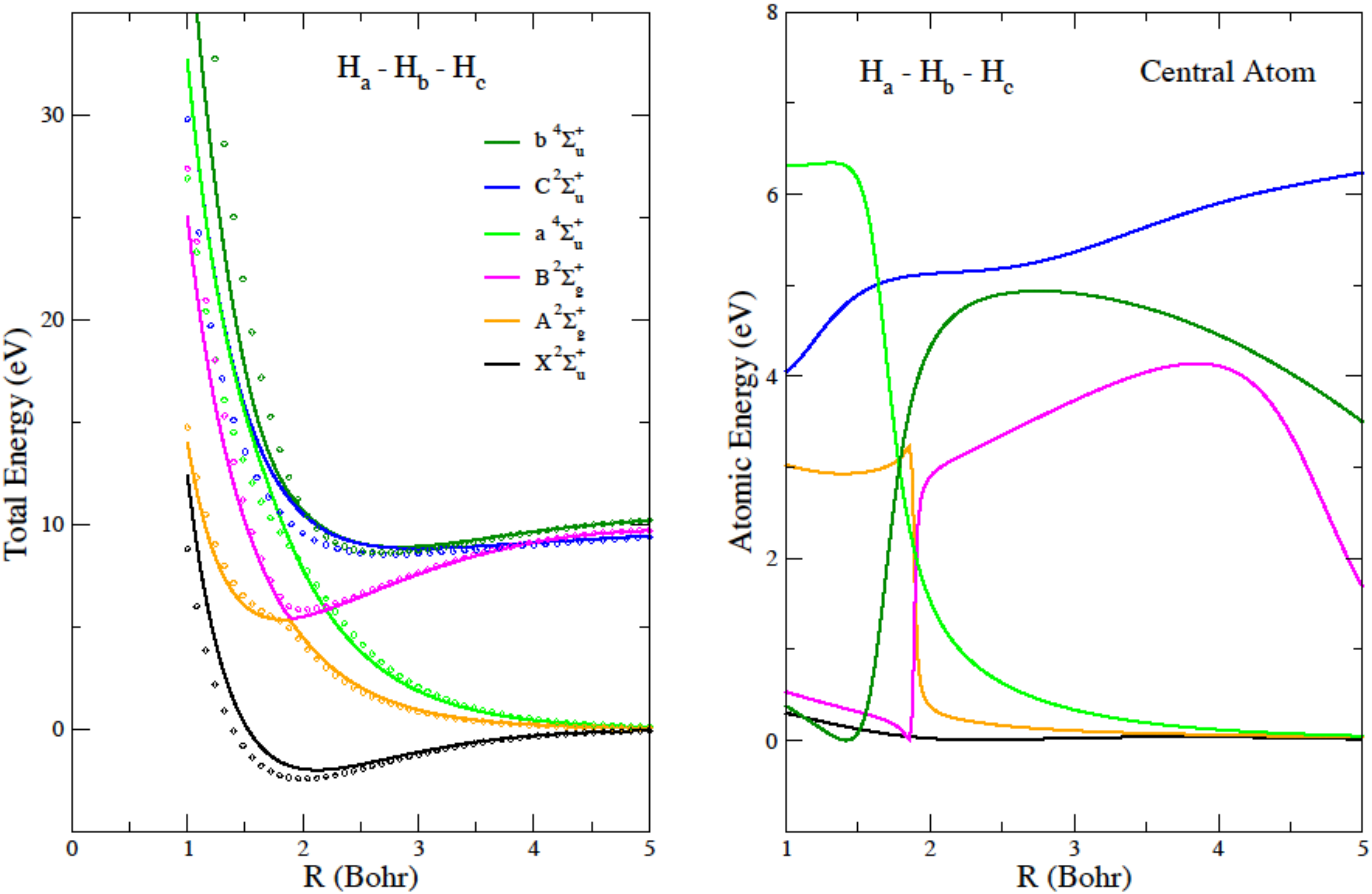
Symmetric Collinear H_3 Molecule



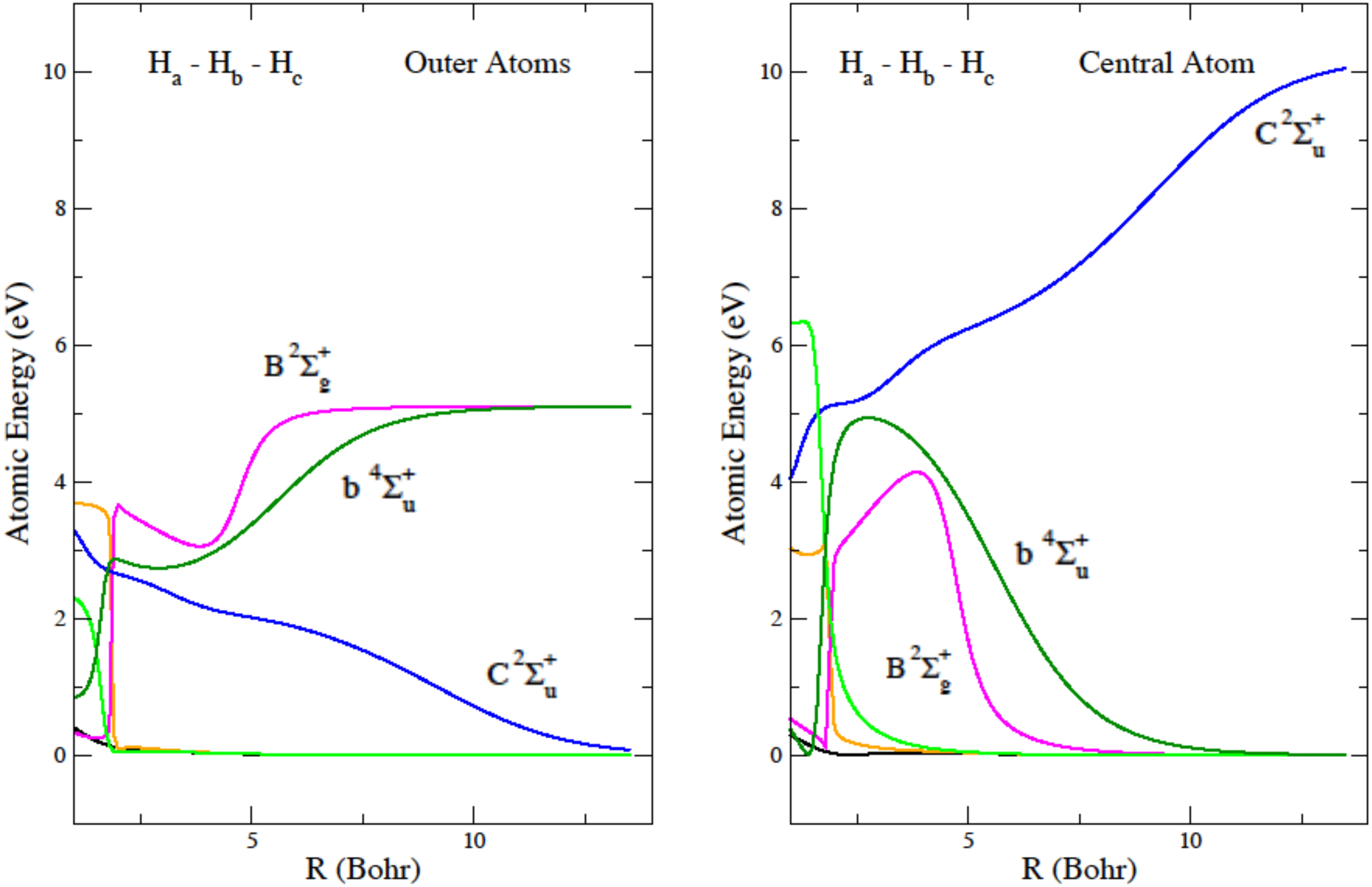
Calculations of total and atomic energies in symmetric collinear H_3

Symmetric Collinear H_3 Molecule



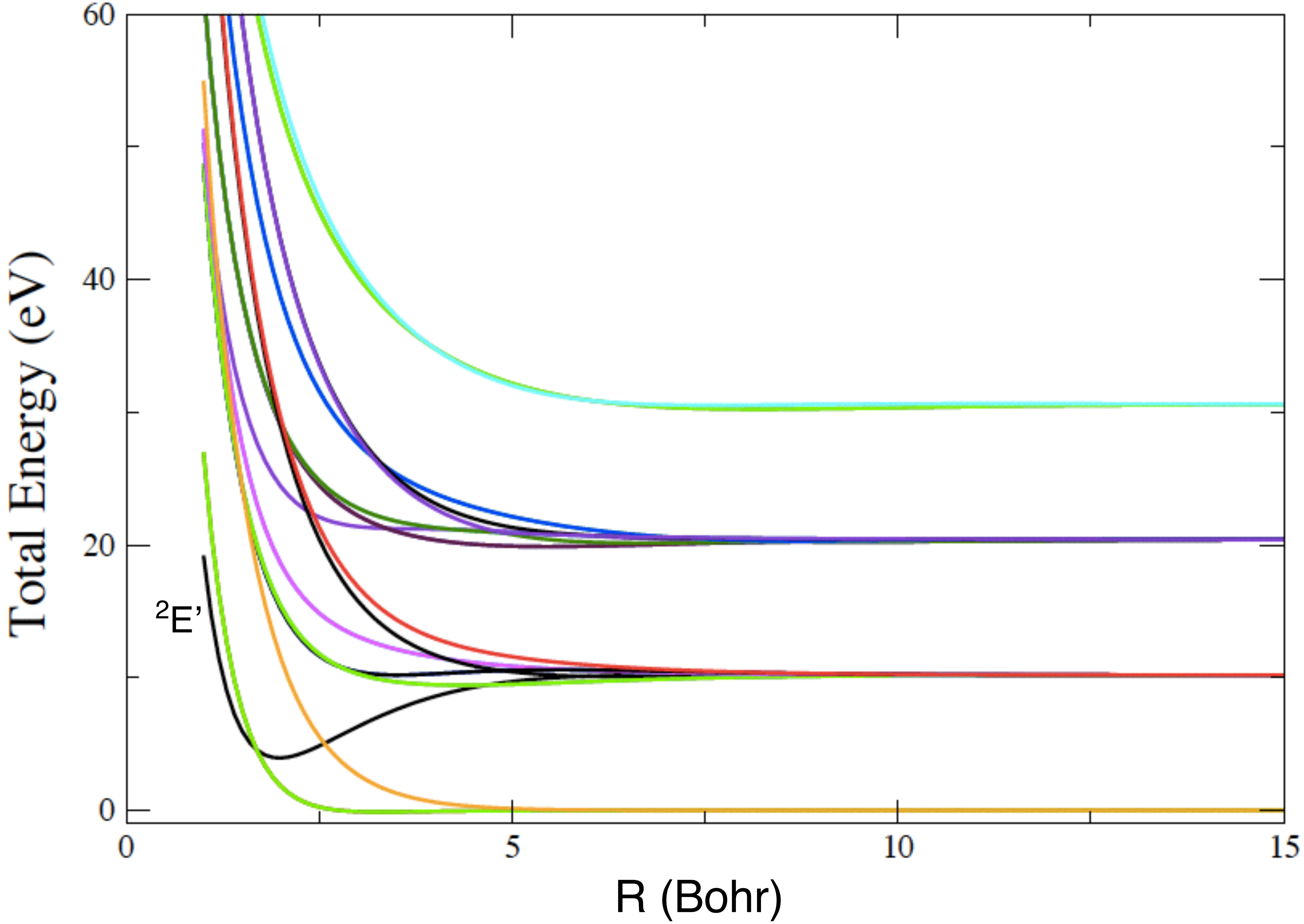
Calculations of total and atomic energies in symmetric collinear H_3

Entanglement in Symmetric Collinear H_3



Calculations of atomic entanglement in symmetric collinear H_3

Total Electronic Energies in Triangular H_3



Calculations of total electronic energies in triangular H_3

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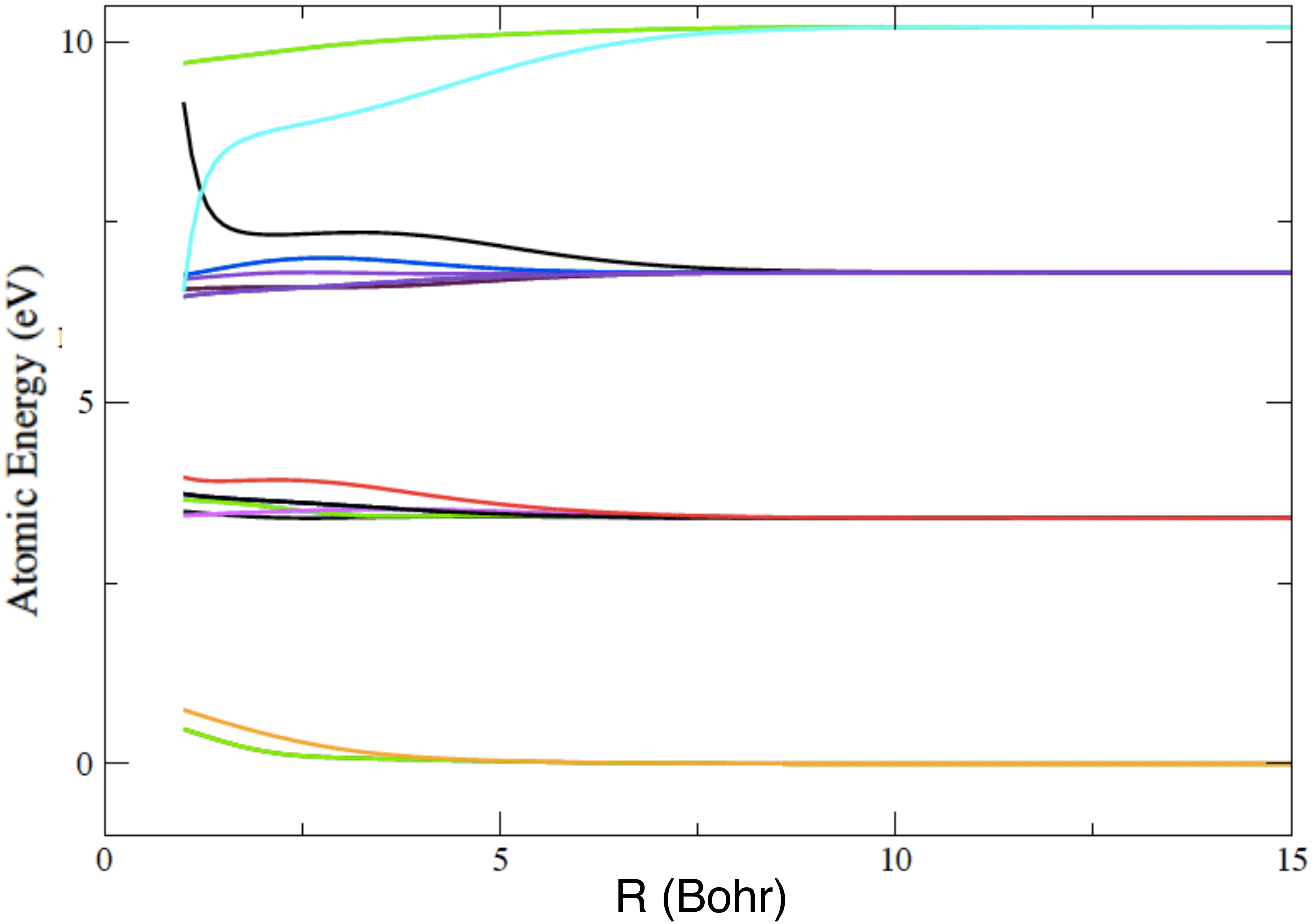
Atomic Entanglement in Triangular H_3



Calculations of atomic energies in triangular H_3

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Summary Remarks

Atomic product representations insure that atoms are well defined in molecules

Total energy surfaces are partitioned into atomic and interaction-energy surfaces

Implementation is provided for calculations in conventional orbital basis sets

Applications describe atomic promotion and interaction energies in H_2/H_3 molecules

Atomic promotion and interaction energies “accommodate” in lowering total energies

The anti-bonding state in H_2 exhibits “attraction” to compensate significant atomic promotion

Electronic charge is distributed through promotion into excited bound atomic states

Atomic interaction energies are potentially measurable on an ultra-fast time scale

Predicted atomic entanglements are measurable upon dissociation of molecular H_3

“The chemical bond is not so simple as some people seem to think.” R.S. Mulliken

The most beautiful experience we can have is the mysterious.

Albert Einstein