Efficient Algorithm for Two-Center Coulomb and Exchange Integrals of Electronic Prolate Spheroidal Orbitals

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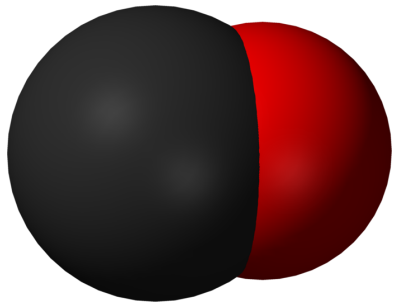
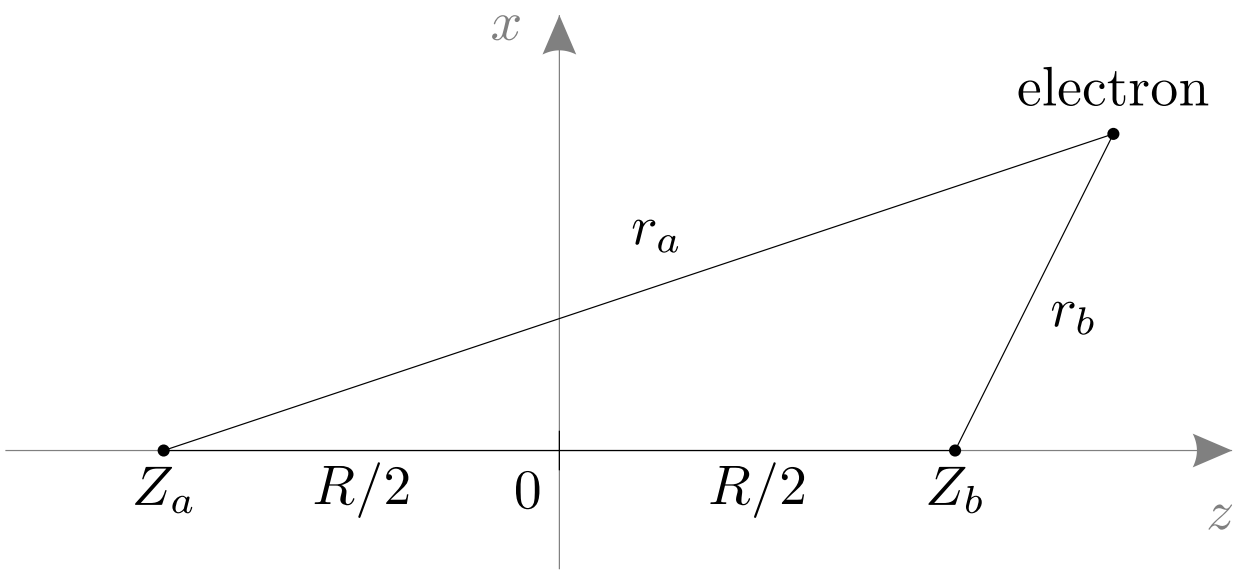
Overview

- Two-center electronic Schrödinger equation for diatomic molecules
- Separable in prolate spheroidal coordinates in the *single*-electron case
- Goal: fast algorithm for the inter-electron Coulomb/exchange integrals of these single-electron wavefunctions



Framework: Single-Electron Schrödinger Equation

$$\left(-\frac{1}{2}\Delta - \frac{Z_a}{r_a} - \frac{Z_b}{r_b}\right)\psi = E\psi \quad (\mathrm{H}_2^+\text{-like ion})$$



Ansatz: $\psi(\xi,\eta,\varphi) = \Lambda(\xi)S(\eta)\frac{e^{\mathbb{i}m\varphi}}{\sqrt{2\pi}}$

$$\xi \in [1,\infty), \eta \in [-1,1], \varphi \in [0,2\pi)$$

Coupled Angular and Radial ODEs

$\rightsquigarrow$ coupled ODEs for the radial part $\Lambda(\xi)$ and angular part $S(\eta)$ (compare with angular spheroidal wave equation):

$$\left[\frac{\partial}{\partial\eta}\left(\left(1-\eta^2\right)\frac{\partial}{\partial\eta}\right)+\underbrace{\left(p^2-A\right)}_{\lambda_\ell^\mu(\mathbb{i}p,\Delta q)}-\Delta q\,\eta+(\mathbb{i}p)^2\left(1-\eta^2\right)-\frac{\mu^2}{1-\eta^2}\right]S(\eta)=0$$

$$\left[\frac{\partial}{\partial\xi}\left(\left(\xi^2-1\right)\frac{\partial}{\partial\xi}\right)-\underbrace{\left(p^2-A\right)}_{\lambda_\ell^\mu(\mathbb{i}p,\Delta q)}+2\,ZR\,\xi+(\mathbb{i}p)^2\left(\xi^2-1\right)-\frac{\mu^2}{\xi^2-1}\right]\Lambda(\xi)=0$$

with $\mu := |m|$, $Z := \frac{Z_a+Z_b}{2}$, $\Delta q := (Z_a - Z_b)\,R$, and

$$\text{energy}\quad E =: -2\,(p/R)^2$$

(Aubert et al. 1974)

Series Expansion of the Wavefunctions

Angular: Legendre polynomials $P_k^\mu(\eta)$:

$$S_\ell^\mu(\mathbb{i}p, \Delta q, \eta) = \sum_{k=\mu}^{\infty} c_{\ell,k}^\mu(p, \Delta q) \left(\frac{2k+1}{2} \frac{(k-\mu)!}{(k+\mu)!} \right)^{1/2} P_k^\mu(\eta)$$

Radial: $\Lambda(\xi) = H_{\mathbf{d}}^\mu(2p\,(\xi - 1))$ with *Hylleraas* functions

$$H_k^\mu(x) := x^{\mu/2} \mathrm{e}^{-x/2} \sqrt{k!/(k+\mu)!}\; L_k^\mu(x), \quad k, \mu \in \mathbb{N}_0,$$

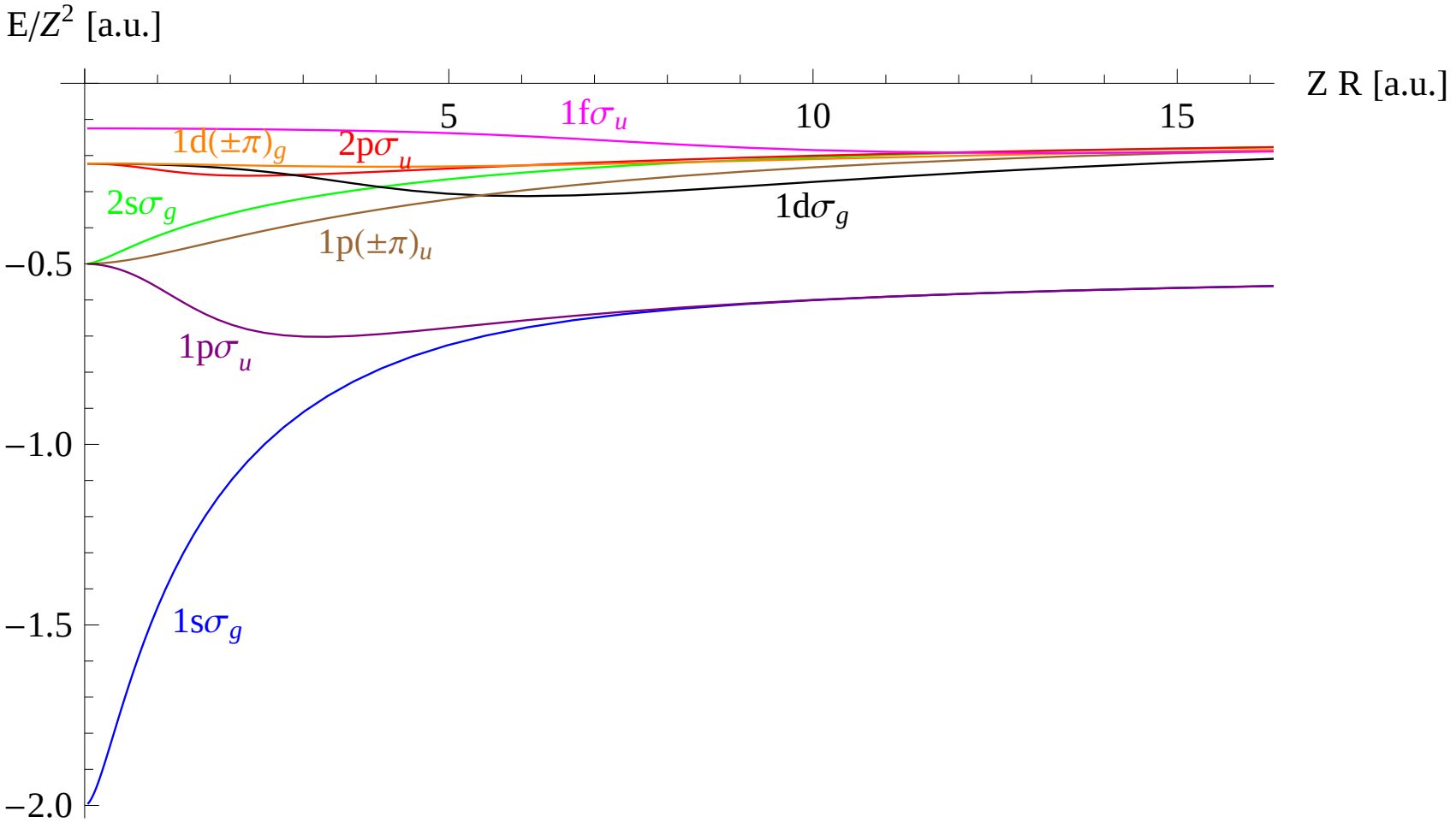
$$H_{\mathbf{d}}^\mu(x) := \sum_{k=0}^{\infty} d_k\, H_k^\mu(x), \quad \mathbf{d} \equiv (d_k)_{k \geq 0}$$

Orthogonality:

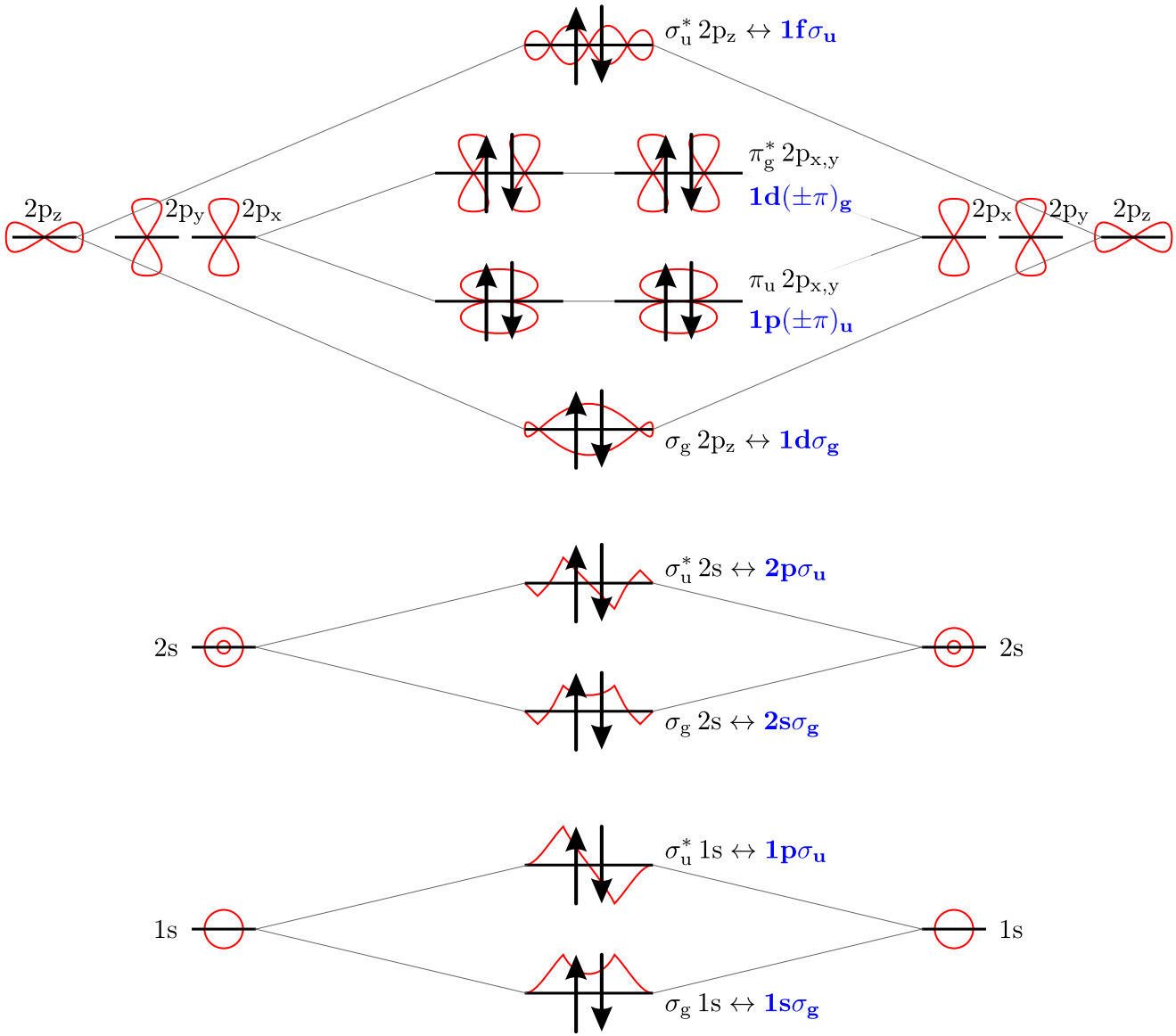
$$\int_0^\infty H_{k'}^\mu(x) H_k^\mu(x)\, \mathrm{d}x = \delta_{kk'}$$

Single-electron Energy Levels

Single-electron energy levels of a H_2^+-like homonuclear dimer



Comparison with "Molecular Orbitals"



Coulomb/Exchange Integrals of Prolate Spheroidal Orbitals

Want to calculate Coulomb/exchange integrals

$$(ab\,|\,cd) := \int_{\mathbb{R}^6} \overline{a(\mathbf{x}_1)} b(\mathbf{x}_1) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \overline{c(\mathbf{x}_2)} d(\mathbf{x}_2)\,\mathrm{d}\mathbf{x}_1\mathbf{x}_2$$

for above single-electron wavefunctions, i.e.,

$$\left(\psi_{n\ell m}\psi_{n'\ell' m'}\,|\,\psi_{\tilde{n}\tilde{\ell}\tilde{m}}\psi_{\tilde{n}'\tilde{\ell}'\tilde{m}'}\right)$$

$\rightsquigarrow$ employ Neumann's expansion of $1/|\mathbf{x}_1 - \mathbf{x}_2|$

Neumann's Expansion of $1/|\mathbf{x}_1 - \mathbf{x}_2|$

$$\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} = \frac{4}{R} \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\tau} (-1)^{\nu} \epsilon_{\nu} \frac{2\tau+1}{2} \left(\frac{(\tau-\nu)!}{(\tau+\nu)!} \right)^2 P_{\tau}^{\nu}(\xi_1) Q_{\tau}^{\nu}(\xi_2) \times P_{\tau}^{\nu}(\eta_1) P_{\tau}^{\nu}(\eta_2) \cos(\nu(\varphi_1 - \varphi_2))$$

for $\xi_1 < \xi_2$ (otherwise interchange $\xi_1 \leftrightarrow \xi_2$)
P_{τ}^{ν} and Q_{τ}^{ν}: Legendre functions of the first and second kind, respectively

$$Q_0^0(\xi) = \operatorname{arcoth}(\xi), Q_1^0(\xi) = -1 + \xi \operatorname{arcoth}(\xi), \ldots$$

Tricky part will be the radial nested integral (due to the dependence of $\xi_1 < \xi_2$ or $\xi_1 \geq \xi_2$)

Nested Radial Coulomb Integrals

$$\int_1^\infty \Lambda_{\tilde{i}}(\xi_2)\Lambda_{\tilde{i}'}(\xi_2)Q_\tau^\nu(\xi_2)\xi_2^{\tilde{j}} \times \int_1^{\xi_2} \Lambda_i(\xi_1)\Lambda_{i'}(\xi_1)P_\tau^\nu(\xi_1)\,\xi_1^j\,\mathrm{d}\xi_1\,\mathrm{d}\xi_2 + \left\langle ii'j \leftrightarrow \tilde{i}\tilde{i}'\tilde{j} \right\rangle$$

for $j, \tilde{j} \in \{0, 2\}$ due to the volume element $(\xi^2 - \eta^2)\,\mathrm{d}\xi\,\mathrm{d}\eta$
First step: set $p_{ii'} := (p_i + p_{i'})/2$ and calculate $\mathbf{d}_{ii'}$ such that

$$\Lambda_i(\xi)\Lambda_{i'}(\xi) \equiv H_{\mathbf{d}_i}^\mu(2p_i\,x)H_{\mathbf{d}_{i'}}^{\mu'}(2p_{i'}\,x) \stackrel{!}{=} H_{\mathbf{d}_{ii'}}^\nu(2p_{ii'}\,x), \quad x := \xi - 1$$

After some intermediate steps: linear combination of

$$b_{\tau,k\tilde{k}}^\nu(z) := \frac{(\tau-\nu)!}{(\tau+\nu)!}\int_0^\infty H_{\tilde{k}}^\nu(\tilde{x})Q_\tau^\nu(1+\tilde{x}/z) \times \int_0^{\tilde{x}} H_k^\nu(x)P_\tau^\nu(1+x/z)\,\mathrm{d}x\,\mathrm{d}\tilde{x} + \left\langle k \leftrightarrow \tilde{k} \right\rangle$$

Explicit Symbolic Integration

$$Q_0^0(1+2x/z) = \operatorname{arcoth}(1+2x/z) = \tfrac{1}{2}\left(\log(1+x/z) - \log(x/z)\right)$$

Proposition

Let $z \in \mathbb{R}_{>0}$ and $y \in \mathbb{R}$, then for all integers $k, \mu \geq 0$,

$$\int_0^\infty \frac{1}{x+z} L_k^\mu(y\,x)\,\mathrm{e}^{-x}\,\mathrm{d}x$$

$$= L_k^\mu(-y\,z)\,\Gamma(0,z)\,\mathrm{e}^z - \frac{1}{z}\sum_{i=1}^{k} h_{ki}^\mu(y)\frac{(y\,z)^i}{i!}$$

with the incomplete gamma function Γ, and

$$h_{ki}^\mu(y) := \sum_{n=i}^{k}(-y)^{n-i}\binom{k+\mu}{n+\mu}\Big/\binom{n}{i}, \quad y \in \mathbb{R}$$

Explicit Symbolic Integration (cont.)

Proposition

Let $z \in \mathbb{R}_{>0}$ and $y \in \mathbb{R}$, then for all integers $k, \mu \geq 0$,

$$\int_0^\infty \log(x/z)\, L_k^\mu(y\,x)\, \mathrm{e}^{-x}\, \mathrm{d}x = \sum_{i=1}^{k} \binom{k+\mu}{i+\mu} (-y)^i H_i$$

$$- \binom{k+\mu}{k} \left((1-y)^k + \mu \sum_{i=1}^{k} \binom{k}{i} \frac{y^i (1-y)^{k-i}}{i+\mu} \right) (\gamma + \log(z)),$$

where H_i is the i^{th} Harmonic number

Products of Laguerre Expansions

- For the above calculations, need to represent products of Laguerre expansions
- Goal: given exponentially decaying sequences $(d_{1,k}), (d_{2,k})$, calculate the sequence (d_k) such that

$$H^{\mu_1}_{\mathbf{d}_1}(x) \cdot H^{\mu_2}_{\mathbf{d}_2}(x) \stackrel{!}{=} H^{\mu_1 \pm \mu_2}_{\mathbf{d}}(x) \quad \forall x \geq 0$$

  with $\mu_1 \geq \mu_2 \geq 0$
- Due to orthogonality relation $\int_0^\infty H^{\mu}_{k'}(x) H^{\mu}_{k}(x)\,\mathrm{d}x = \delta_{kk'}$, this leads to integrals of the form

$$\int_0^\infty H^{\mu_1}_{i_1}(x) H^{\mu_2}_{i_2}(x) H^{\mu_3}_{i_3}(x)\,\mathrm{d}x$$

Products of Laguerre Expansions (cont.)

Proposition

Given fixed integers $\boldsymbol{\mu} \in \mathbb{N}_0^3$, *the coefficients*

$$c_{\mathbf{i}}^{\boldsymbol{\mu}}(z) := \int_0^\infty L_{i_1}^{\mu_1}(x) L_{i_2}^{\mu_2}(x) L_{i_3}^{\mu_3}(x)\, \mathrm{e}^{-z\,x}\, \mathrm{d}x, \quad z \in \mathbb{R}_{>0}$$

defined for $\mathbf{i} \in \mathbb{N}_0^3$ *obey the recurrence relation*

$$\begin{aligned} c_{\mathbf{i}}^{\boldsymbol{\mu}}(z) = &- (1/z - 1) \left(c_{i_1-1,i_2,i_3}^{\boldsymbol{\mu}}(z) + c_{i_1,i_2-1,i_3}^{\boldsymbol{\mu}}(z) + c_{i_1,i_2,i_3-1}^{\boldsymbol{\mu}}(z) \right) \\ &+ (2/z - 1) \left(c_{i_1,i_2-1,i_3-1}^{\boldsymbol{\mu}}(z) + c_{i_1-1,i_2,i_3-1}^{\boldsymbol{\mu}}(z) + c_{i_1-1,i_2-1,i_3}^{\boldsymbol{\mu}}(z) \right) \\ &- (3/z - 1) c_{i_1-1,i_2-1,i_3-1}^{\boldsymbol{\mu}}(z) + \frac{1}{z} \prod_{k=1}^{3} \binom{\mu_k - 1 + i_k}{i_k} \end{aligned}$$

with the convention that $c_{\mathbf{i}}^{\boldsymbol{\mu}}(z) = 0$ *if any* $i_1, i_2, i_3 < 0$ *and* $\binom{i-1}{i} = \delta_{0i}$ *for integer* $i \geq 0$.

Sketch of the Proof

Similar to Lord (1960), use generating functions of Laguerre polynomials:

$$\sum_{i=0}^{\infty} L_i^{\mu}(x)(-t)^i = \frac{\mathrm{e}^{x\,t/(1+t)}}{(1+t)^{\mu+1}}, \quad \text{thus}$$

$$G^{\boldsymbol{\mu}}(t_1,t_2,t_3,z) := \sum_{i_1,i_2,i_3=0}^{\infty} c_{\mathbf{i}}^{\boldsymbol{\mu}}(z) \prod_{k=1}^{3}(-t_k)^{i_k} = z^{-1}\frac{\prod_{k=1}^{3}(1+t_k)^{-\mu_k}}{1-p(t_1,t_2,t_3,z)},$$

$$\begin{aligned} p(t_1,t_2,t_3,z) &:= (1/z-1)\,(t_1+t_2+t_3) \\ &\quad + (2/z-1)\,(t_1t_2+t_1t_3+t_2t_3) + (3/z-1)t_1t_2t_3. \end{aligned}$$

Using $1/(1-x) = 1 + x/(1-x)$ for $x = p(t_1,t_2,t_3,z)$ leads to

$$G^{\boldsymbol{\mu}}(t_1,t_2,t_3,z) = p(t_1,t_2,t_3,z)\,G^{\boldsymbol{\mu}}(t_1,t_2,t_3,z) + \frac{1}{z}\prod_{k=1}^{3}(1+t_k)^{-\mu_k}.$$

Finally, compare coefficients of $t_1^{i_1}\,t_2^{i_2}\,t_3^{i_3}$.

Application to Diatomic Molecules

N-electron Hamiltonian for diatomic molecules:

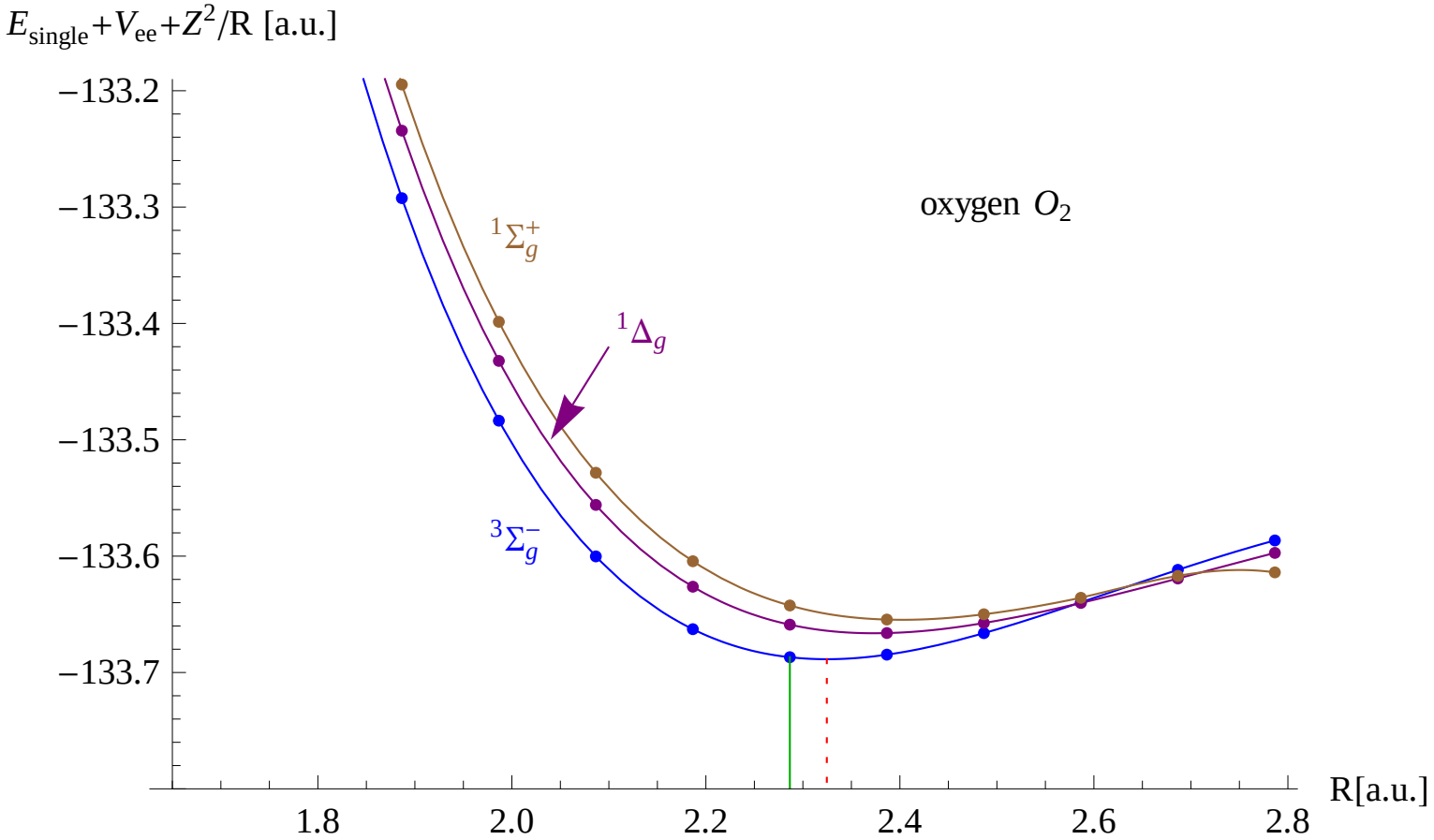
$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z_a}{r_{ia}} - \frac{Z_b}{r_{ib}} \right) + \sum_{i<j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \frac{Z_a Z_b}{R}$$

Discretization by antisymmetrized products of single-electron wavefunctions, i.e., Ansatz space $\wedge^N V_{\text{single}}$ with

$$V_{\text{single}} := \text{span}\left\{ \psi\uparrow, \psi\downarrow : \left(-\frac{1}{2}\Delta - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} \right) \psi = E\psi, E \leq E_{\text{max}} \right\}$$

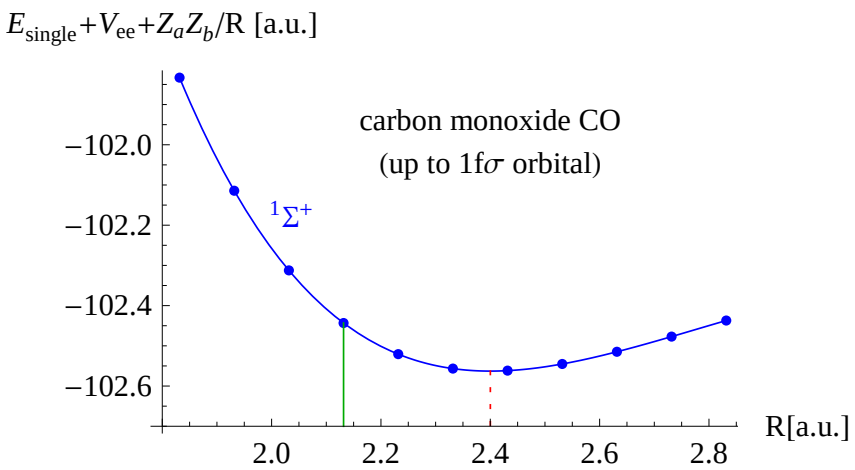
Oxygen Molecule O_2

Paramagnetic "triplet" oxygen molecule O_2 (groundstate symmetry ${}^3\Sigma_g^-$)
Express $\langle \Psi_i \,|\, V_{\text{ee}}\, \Psi_j \rangle$ as linear combination of $\left(\psi_{n\ell m}\psi_{n'\ell' m'} \,|\, \psi_{\tilde{n}\tilde{\ell}\tilde{m}}\psi_{\tilde{n}'\tilde{\ell}'\tilde{m}'}\right)$:
FermiFab software toolbox (Mendl 2011, 2012)

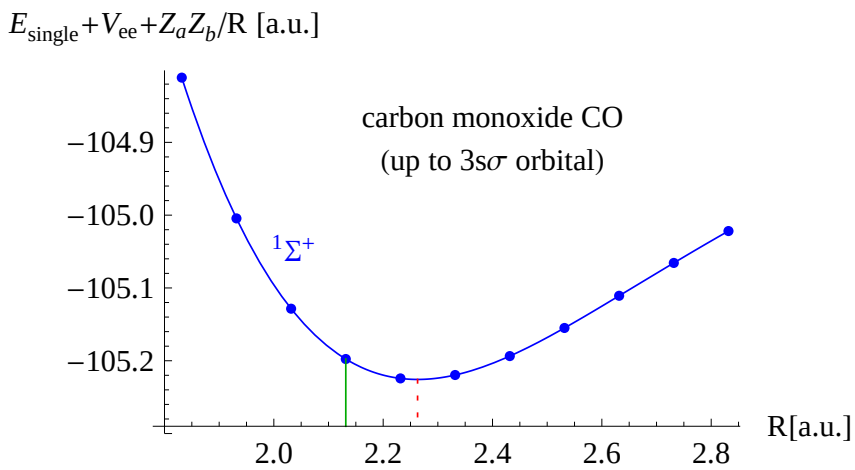


Carbon Monoxide CO

Heteronuclear molecule CO ($Z_a = 8$, $Z_b = 6$ and $N = 14$)



(a) up to $1f\sigma\uparrow\downarrow$ subshell



(b) additionally including $3s\sigma\uparrow\downarrow$

Summary

- Efficient computational framework to evaluate Coulomb/exchange integrals in prolate spheroidal coordinates
- Employing Neumann's expansion of $1/|\mathbf{x}-\mathbf{y}|$
- Reproduce qualitatively correct energy curves and bond lengths of O_2 and CO as model problems (even for small number of single-electron wavefunctions)
- Can precompute integrals, universal for other molecules

References

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