Linearized approach to relativistic minimax (LARM) for many-particle systems

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Basic relativity problem

Approximation of electron solutions only by
projection against negative continuum:

(i) via bound states **boundary conditions**. **Non-linear** in the eigenvalue, **not** energy optimized.

Energy optimized, minimize $I^{(4)} = < \psi | H - E | \psi >$:

(ii) via **pre-projected** relativistic AOs in LCAO. **Linear** in the eigenvalue, semi-convergent, artifacts.

(iii) via **orthogonality** against a discretized negative continuum from a systematic basis (FEM, STOs, GTOs, wavelets, etc.). **Linear** in eigenvalue, slowly convergent, artifacts.

(iv) via the relativistic **Minimax** formalism. **Non-linear** in eigenvalue. Linear approximations to it **(Kinetic, T-V and T-V-D balance)**, **linear** in eigenvalue, **weighted** discretization of negative continuum.

Minimax principle and its linear approximations

Minimax functional: $I_{\text{minimax}} = \int \frac{\hbar^2 |\hat{L}\psi_L|^2}{2m + (E-V)/c^2} dr^3 + \int (V-E)\,|\psi_L|^2 dr^3$

Linear functionals: $I^{(2)} = < \psi | T + V - E | \psi >$ with

$$\psi = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix}, \qquad \psi_L = \sum_j a_j \chi_j^{AO,L}$$

(a) Kinetic Balance (KB): $\psi_S = \sum_j b_j \frac{\hat{L}\chi_j^{AO,L}}{2mc^2}$,

(b) Kinetic and Potential Balance (TVB): $\psi_S = \sum_j b_j \frac{\hat{L}\chi_j^{AO,L}}{E_0 + 2mc^2 - V}$

(c) Kinetic and Potential Defect Balance (TVDB):

$$\psi_S = \frac{\hat{L}\psi_L}{E_0 + 2mc^2 - V} + \sum_j b_j \frac{\hat{L}\chi_j^{AO,L}}{(E_0 + 2mc^2 - V)^2}$$

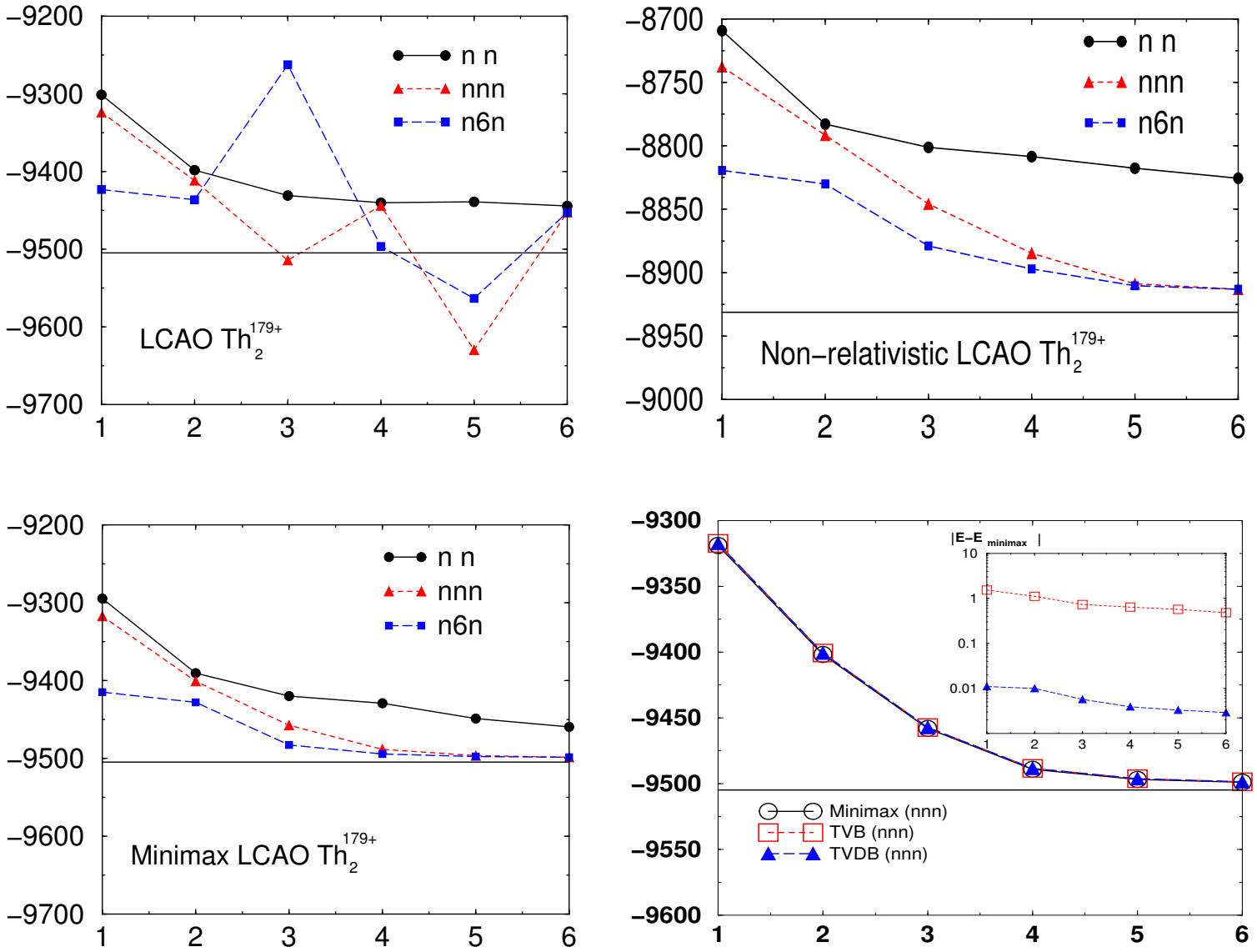

Figure: Convergence pattern of the ground state energies for different schemes. Scaled H_2^+ distance, normal monopole potential for AOs.

Extension to many-particle systems

SCF calculations (DFT, Dirac-Fock, etc.) for many-body systems. Two basic problems:

(i) The self consistent potential in the denominator of Minimax, non-local for Dirac-Fock. Solution: Replace V_{SCF} in the denominator of the small component basis for TVB (TVDB) with a suitable fixed potential V_{fix} .

(ii) One has to treat multi-centered integrals like

$$\int V_{\mathsf{SCF}}(\mathbf{r}) \frac{\hat{L}\phi_i^+(\mathbf{r})}{E_0 + 2mc^2 - V_{\mathsf{fix}}(\mathbf{r})} d^3r.$$

Possible solutions:
Numerical integration in 3D (Code available for LCAO).
Or re-fit small component basis with given functions.

References

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[5] H. Zhang, H. J. Luo, J. Kolb, O. Kullie and D. Kolb, *Linear approximation to relativistic Minimax (LARM) applied to a LCAO description of the two-center Coulomb problem*, preprint 2005, submitted J. Phys. B: At. Mol. Opt. Phys.

Table: Spectrum of $J_z = 1/2$ states Th_2^{179+} ($R = 2/90$ a.u.) up to $n = 6$. s marks spurious. $E_0 = -4000$ a.u. Smoothed monopole potential for AOs.

No.	4-SP LCAO	KIN-B	T-V-B	T-V-D-B	MINIMAX	FEM
	-36176 s					
	-32671 s					
	-31246 s					
	-24182 s					
	-19086 s					
	-12354 s	-15447 s				
	-10777 s	-13673 s				
1	-9510.50	-8940	-9503.79	-9503.5550	-9503.5538	-9504.757
		-8306 s				
2	-6813.20	-6625	-6814.669	-6814.643698	-6814.643653	-6815.513
	-5850 s					
3	-4126.48	-4032	-4126.787789	-4126.7877545	-4126.7877544	-4127.891
	-4028 s					
4	-3374.23	-3326	-3373.5264	-3373.5258181	-3373.5258177	-3374.520
5	-2563.11	-2706	-2563.8015	-2563.8000129	-2563.8000122	-2564.181
6	-2457.08	-2547	-2455.313	-2455.309632	-2455.309631	-2455.956
		-2033 s				
7	-2010.01	-2004	-2010.4425	-2010.4417540	-2010.4417536	-2010.664
8	-1917.072	-1892	-1916.4569	-1916.452865	-1916.452860	-1917.124
9	-1655.06	-1640	-1652.3456	-1652.342807	-1652.342803	-1652.815
	-1352 s					
10	-1336.46	-1331	-1336.5135	-1336.511389	-1336.511386	-1336.674
11	-1292.28	-1283	-1329.9359	-1329.930772	-1329.930766	-1330.255
	-1173 s					
12	-1138.42	-1135	-1138.8245	-1138.823465	-1138.823463	-1138.978
13	-1105.162	-1104.1	-1105.03453	-1105.034188	-1105.034187	-1105.112
14	-1084.36	-1075	-1083.8081	-1083.804519	-1083.804512	-1084.182
15	-1055.780	-1055.776	-1055.781472	-1055.7814692	-1055.7814692	-1055.802
16	-965.69	-962	-966.3824	-966.380320	-966.380316	-966.6071
17	-819.154	-813	-818.9833	-818.979608	-818.979601	-819.1415

Defect correction formulation

Hybrid bases {AOs, systematic basis}

$$\psi_i^{(k)} = a_{i,0}^{(k)} \sum_j a_{i,j}^{(k-1)} \phi_j^{\mathrm{LCAO}} + \sum_l f_{i,l}^{(k)} N_l$$

– Determine $a_{i,0}^{(k)}, f_{i,l}^{(k)}$ via minimization of I_{minimax} ($I^{(2)}$,$I^{(4)}$) for fixed $\{a_{i,j}^{(k-1)}\}$.

– Update $a_{i,j}^{(k-1)}$ by orthogonalization of $\{\psi_i^{(k)}\}$.

– The converged solution minimizes I_{minimax} ($I^{(2)}$,$I^{(4)}$) in full hybrid space.

Table: Total energy of the C_2-molecule for a DKM- calculation with varying numbers of FEM points. The upper index in E_{tot}^b gives the number of atomic basis functions.

points	E_{tot}^{20} [a.u.]	E_{tot}^{44} [a.u.]	E_{tot}^{56} [a.u.]	E_{tot}^{FEM} [a.u.]
441	**-74.92** 305949	**-74.92** 293025	**-74.92** 293934	**-74.9** 7660961
961	**-74.921** 30663	**-74.921** 30492	**-74.921** 30455	**-74.92** 218717
1681	**-74.9212** 2501	**-74.9212** 2490	**-74.9212** 2475	**-74.9212** 8880
2601	**-74.921217** 50	**-74.921217** 49	**-74.921217** 39	**-74.9212** 2327
3721	**-74.921216** 93	**-74.921216** 93	**-74.921216** 84	**-74.92121** 820
LCAO	-74.7831	-74.8961	-74.9047	
exact	**-74.9212172** 5	**-74.9212172** 5	**-74.9212172** 5	**-74.9212172** 5