The DFT LCAO B-spline code

P. Decleva

Università di Trieste, DSCF & CNR-IOM & INSTM
Basic problem: obtain one-particle continuum wavefunctions

\[ h \phi_E = E \phi_E \quad E > 0 \quad (h \phi_i = E_i \phi_i \text{ are easier}) \]

Polyatomic molecules: full 3-D problem

- Coulomb singularities \( V_N(r) = \sum_i -Z_i / |r - R_i| \) at nuclear positions \( R_i \)

- The solution generally has a complicated nodal pattern, both radial and angular

- Large (\( \infty \)) degeneracy: natural truncation on angular momentum

\[ \phi_{Ej} \rightarrow \sum_{lm} R_{ilm}(r) Y_{lm}(\theta,\phi) \quad l \leq L_{\text{max}} \quad , \quad j = 1, N_o \]
Ca@C60  \(1a_g \rightarrow t_{1u}\)
Basis set approach

\[ \varphi_E = \sum_\mu \chi_\mu \mathcal{C}_{\mu E} \]

The main issue is proper basis set choice

\[ \chi_{ilm} = \frac{1}{r} B_i(r) Y_{lm}(\vartheta, \varphi) \]
B- splines

- A numerical analyst toolkit, can approximate any reasonably smooth function
- Fast convergence
- Excellent conditioning
- Any boundary condition easily satisfied
- Strong locality, sparse matrices
- Complete (as a function of the knot sequence)
- Offer local control of resolution
- Self similarity
- For most operators, easy evaluation of matrix elements

  Matrix evaluation on the fly? \( b = H c \)
One Center Expansion: \( \{\chi_\mu^o\} \)

Multicenter expansion: \( \{\chi_\mu^p\} \)
One center expansion (OCE): \( \{ \chi_\mu(r_0) \} \)
All functions centered on a common origin 0

Multicenter expansion (LCAO)
\[
\{ \chi_\mu(r_0) \} \cup \{ \chi_\mu_1(r_1) \} \cup \ldots \cup \{ \chi_\mu_p(r_p) \}
\]

OCE: very stable and robust, shows smooth but slow convergence with \( L_{\text{MAX}0} \)

LCAO: converges much more quickly, but less stable, careful choice of numerical parameters. The basis becomes easily overcomplete

Fully symmetry adapted basis
\[
\chi_{i, lh}^{p\mu} = \frac{1}{r} B_i(r) X_{lh}^{p\mu}(\vartheta, \varphi) \quad X_{lh}^{p\mu} = \sum_m b_{lh,m}^{p\mu} Y_{lm}^{R}(\vartheta, \varphi)
\]
Basis set approach: introduce a basis \( \{ \chi_\mu \} \)

**Functional equations**

\[
Lf = \lambda f \quad \text{eigenvalue} \quad (\text{e.g. Schroedinger})
\]

\[
Lf = g \quad \text{inhomogeneous} \quad (\text{e.g. Poisson, Dalgarno, ...})
\]

are converted into algebraic equations

\[
f = \sum_\mu \chi_\mu c_\mu \quad \quad L_{\mu \nu} = \langle \chi_\mu \mid L \mid \chi_\nu \rangle \quad \quad S_{\mu \nu} = \langle \chi_\mu \mid \chi_\nu \rangle
\]

\[
Lc = \lambda Sc
\]

\[
Lc = Sd
\]

Spectral methods, numerically accurate and stable algorithms, fast convergence, can adapt to local coordinate systems.

(Very well suited to parallel supercomputers)
In the basis \( H_c = ES_c \)

\[
H_{\mu\nu} = \langle \chi_\mu | H | \chi_\nu \rangle \quad S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle
\]

Bound states: standard diagonalization

Continuum states: Least Squares Approach

\[
\min || (H - E)\Psi ||_R^2 \Rightarrow A^+ Ac = ac
\]

\[
A(E) = H - ES, \quad N_0 \text{ lowest eigenvalues } a_i \approx 0
\]

Works fine, even with \( N_0 \) a few hundred

Linear algebra formulation, ideally suited to supercomputers
For the continuum

- Full multichannel solution at each selected energy
- Convergent results, no approximations on the potential
- High (arbitrary) energy resolution
- High energy limit (E_{max} limited by radial step size)
- Large systems, to fit inside a spherical box, R_{max} \sim 1 \text{ nm}?

Solves the 1-electron problem completely
Figure 13. Detail of the $-l_3$ ($2p3d$) $^1P^o$ resonance. Calculated data are reported as circles and the full curve represents the best fit to data with a Fano profile employing the parameters reported in table 5.
CH4 \sigma_{1t2} electron KE (au)

CH4 \beta_{1t2} electron KE (au)

\textsuperscript{3}\sigma_g

calculation from [6]
grey data points with
thin error bars are from
various other authors [7-9]
The “simple” single particle continuum problem

\[ h \varphi_{E_j} = \varphi_{E_j} \quad 3D, \text{multichannel} \Rightarrow \text{B-splines get it accurately} \]

The many-particle problem (still only 1 electron asymptotically free)

Close Coupling

\[ \Psi_{EJ}^N = \sum_{I}^{\text{open}} \Phi_{I}^{N-1} \varphi_{EIJ} + \sum_{K} C_{K} \Phi_{K}^{N} \]

if a finite number of open channels it is in principle exact, can be extended to FCI for 2 (3, 4?) electrons

Approximations

IPA

\[ \Psi_{Ei}^N = \Phi_{i}^{N-1} \varphi_{Ei} = | \varphi_1 \ldots \varphi_{i-1} \varphi_{Ei} \ldots \varphi_N \rangle \]

SCI

\[ \Psi_{Eij}^N = \sum_{i} \Phi_{i}^{N-1} \varphi_{Eij} \]
DFT: Single Channel

\[ \Psi_{E_i}^N = \Phi_{i}^{N-1} \varphi_{E_i} = | \varphi_1 ... \varphi_{i-1} \varphi_{E_i} ... \varphi_N \rangle \]

\[ h_0 \varphi_i = \varepsilon_i \varphi_i \]
\[ h_0 = -\frac{1}{2} \Delta + V_N + V_C(\rho) + V_{XC}(\rho) \]
\[ \Delta V_{C}(\rho) = -4\pi \rho \]
\[ V_{XC}(r) = V_{XC}(\rho(r)) \]

TDDFT: Coupled Channel

\[ \Psi_{EJ}^N = \sum_i \Phi_{i}^{N-1} \varphi_{Eij} \]

\[ \{ h_0 + V_{\text{eff}} \} \varphi_i(t) = i \partial \varphi_i / \partial t \]
\[ V_{\text{eff}}(t) = V_{\text{ext}}(t) + V_C(\delta \rho) + V_{XC}(\delta \rho) \]

to first order

\[ \varphi_i(t) = \varphi_i + \varphi_i^{(+)} e^{i\omega t} + \varphi_i^{(-)} e^{-i\omega t} \]

\[ \Rightarrow \quad (h_0 - \varepsilon_i \pm \omega) \varphi_i^{(\pm)} = -Q V_{\text{eff}}^{(\pm)} \varphi_i \]
Matrix approach (1h-1p space, dimension is NOCC × NDIM)

\[ \varphi_i^{(-)} = \sum_a \varphi_a X_{ai} \quad \varphi_i^{(+)} = \sum_a \varphi_a Y_{ai}^* \]

\[ \Rightarrow \quad A X + B Y = \omega X \]

\[ B^* X + A^* Y = -\omega Y \]

RPA is formally identical, with

\[ A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + \langle aj||ib \rangle = \langle \Phi_i^a||H-E_0|| \Phi_j^b \rangle \]

\[ B_{ia,jb} = \langle ab||ij \rangle = \langle \Phi_{ij}^{ab}||H-E_0|| \Phi_0 \rangle \]

RPA → TDDFT

\[ \varepsilon_i^{(HF)} \rightarrow \varepsilon_i^{(DFT)} \]

\[ \langle ab||ij \rangle \rightarrow \langle ab||ij \rangle + \langle ab||W^{\sigma_i\sigma_j}||ij \rangle \]

\[ W^{\sigma_i\sigma_j} = \frac{\partial^2 E_{XC}}{\partial \rho_{\sigma_i} \partial \rho_{\sigma_j}} \]
Direct approach, non iterative

\[ \delta V = K \delta \rho \]
\[ \delta \rho = \chi V_{SCF} \]
\[ V_{SCF} = V_{ext} + \delta V \]
\[ (K\chi - 1)V_{SCF} = -V_{ext} \leftarrow \text{Basic equation} \]

Expand all quantities in the basis

\[ \langle \lambda | K\chi | \mu \rangle = \sum ( -4\pi \Delta^{-1} + \frac{\partial V_{XC}}{\partial \rho} S^{-1})_{\lambda \nu} \langle \nu | \delta \rho | \mu \rangle \]

Where \( \delta \rho | \mu \rangle \) is the density induced by a perturbing potential given by the basis function \(| \mu \rangle \)

- Compute \( (S^{-1})_{\lambda \nu}, (\Delta^{-1})_{\lambda \nu}, (\partial V_{XC}/\partial \rho)_{\lambda \nu} \)
- Solve the PT equations for each \(| \mu \rangle \), obtain \( \partial \rho | \mu \rangle, < \mu | \partial \rho | \mu \rangle \)
- Compute \( < \lambda | K\chi | \mu > \) and solve for \( V_{SCF} \)
- Obtain \( \phi_{i}^{(\pm)} \) given \( V_{SCF} \)

NDIM x NDIM matrices
COMPUTATIONAL STEPS

a. Given initial density $\rho$ compute molecular potential

$$V_N + V_C + V_{XC},$$

and matrix elements $<\chi_\mu, (V_N + V_C + V_{XC}) \chi_\nu>$

- compute $<\chi_\mu, \rho>$

- solve Poisson equation $\Delta V_C = -4\pi \rho$

$$\Rightarrow Ac = b \quad \text{linear system in the same basis}$$
- compute scalar products by numerical integration

\[
< f, g > = \int f(r) g(r) \, dr = \sum_i w_i f(r_i) g(r_i)
\]

b. Set up \( H_{\mu\nu}, S_{\mu\nu} \) (block cyclic decomposition)

set up \( H^H, (H^H S + S^H H), S^H S \) (id.)

c. For each energy build \( A^+A = H^H - E(H^H S + S^H H) + E^2 S^H S \),

perform LU decomposition and solve \( A^+A \, c = a \, c \) by inverse iteration (SCALAPACK)

d. Compute transition moments

\[
d_{fi} = < \Psi_f, D \Psi_i > = c_f^+ D c_i
\]
<table>
<thead>
<tr>
<th>SORTED R</th>
<th>RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.61064250375</td>
</tr>
<tr>
<td>2</td>
<td>2.18406104737</td>
</tr>
<tr>
<td>3</td>
<td>2.62975976097</td>
</tr>
<tr>
<td>4</td>
<td>3.16754881097</td>
</tr>
<tr>
<td>5</td>
<td>3.639084701767</td>
</tr>
<tr>
<td>6</td>
<td>3.94358410597</td>
</tr>
<tr>
<td>7</td>
<td>3.92128658677</td>
</tr>
<tr>
<td>8</td>
<td>3.926919690838</td>
</tr>
<tr>
<td>9</td>
<td>4.29158709207</td>
</tr>
<tr>
<td>10</td>
<td>4.37851222676</td>
</tr>
<tr>
<td>11</td>
<td>4.672682405251</td>
</tr>
<tr>
<td>12</td>
<td>4.67235326263</td>
</tr>
<tr>
<td>13</td>
<td>4.67235987436</td>
</tr>
<tr>
<td>14</td>
<td>4.882174188037</td>
</tr>
<tr>
<td>15</td>
<td>4.887424989568</td>
</tr>
<tr>
<td>16</td>
<td>4.985903557616</td>
</tr>
<tr>
<td>17</td>
<td>5.00510237841</td>
</tr>
<tr>
<td>18</td>
<td>5.005378273224</td>
</tr>
<tr>
<td>19</td>
<td>5.102605865753</td>
</tr>
<tr>
<td>20</td>
<td>5.463613529429</td>
</tr>
<tr>
<td>21</td>
<td>5.471635390995</td>
</tr>
<tr>
<td>22</td>
<td>5.482065031161</td>
</tr>
<tr>
<td>23</td>
<td>5.61394617364</td>
</tr>
<tr>
<td>24</td>
<td>5.650494662275</td>
</tr>
<tr>
<td>25</td>
<td>6.09339075549</td>
</tr>
<tr>
<td>26</td>
<td>6.155765198566</td>
</tr>
<tr>
<td>27</td>
<td>6.202321843613</td>
</tr>
</tbody>
</table>
Computational cost is determined by matrix dimension:

\[ \text{NDIM} \sim \text{NSPL0} \cdot \text{LMAX0}^2 / \text{nsym} \]

\[ \text{NSPL0} \sim 100 \div 200 \text{ is convergent for 1 photon photoionization} \]

\[ \text{CM} = \text{NDIM}^2 \sim \text{LMAX0}^4 \]

\[ \text{CPU} = \text{NDIM}^3 \sim \text{LMAX0}^6 \]

*Convergence is dominated by LMAX0 of OCE expansion*

LMAX0 determined by:

- Short range convergence (much reduced with LCAO)

- Long range convergence, number of waves active at the highest E:
### LMAX0

<table>
<thead>
<tr>
<th>E \ R</th>
<th>5.</th>
<th>10.</th>
<th>20.</th>
<th>a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>12</td>
<td>22</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>24</td>
<td>44</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

#### Number of angular functions in different symmetries

<table>
<thead>
<tr>
<th>Group</th>
<th>$C_1$</th>
<th>$C_{2v}$</th>
<th>$D_{3h}$</th>
<th>$D_{6h}$</th>
<th>$O_h$</th>
<th>$I_h$</th>
<th>$D_{\infty h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMAX0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>121</td>
<td>36</td>
<td>22</td>
<td>12</td>
<td>9</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>441</td>
<td>121</td>
<td>77</td>
<td>40</td>
<td>30</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>40</td>
<td>1681</td>
<td>441</td>
<td>287</td>
<td>147</td>
<td>110</td>
<td>87</td>
<td>21</td>
</tr>
<tr>
<td>80</td>
<td>6561</td>
<td></td>
<td></td>
<td></td>
<td>420</td>
<td>287</td>
<td>41</td>
</tr>
</tbody>
</table>
NSPL0 = 150

<table>
<thead>
<tr>
<th>NDim</th>
<th>NANGF</th>
<th>C1</th>
<th>C2v</th>
<th>D3h</th>
<th>Oh</th>
<th>1 matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>75000</td>
<td>500</td>
<td>22</td>
<td>42</td>
<td>54</td>
<td>&gt;80</td>
<td>45GB</td>
</tr>
<tr>
<td>150000</td>
<td>1000</td>
<td>31</td>
<td>60</td>
<td>80</td>
<td></td>
<td>180GB</td>
</tr>
<tr>
<td>300000</td>
<td>2000</td>
<td>44</td>
<td>70</td>
<td>&gt;80</td>
<td></td>
<td>720GB</td>
</tr>
</tbody>
</table>

NSPL0 = 1500

<table>
<thead>
<tr>
<th>NDim</th>
<th>NANGF</th>
<th>C1</th>
<th>C2v</th>
<th>D3h</th>
<th>Oh</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>300000</td>
<td>200</td>
<td>14</td>
<td>25</td>
<td>33</td>
<td>720GB</td>
<td></td>
</tr>
</tbody>
</table>

With a local block size $\sim 6000 - 10000 \rightarrow 1000 - 2500$ CPU
### Timing (CPU seconds)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>SP3</th>
<th>$D_{2h}$</th>
<th>SP4 (16CPUs)</th>
<th>$O_h$</th>
<th>ratio</th>
<th>SP5</th>
<th>ratio</th>
<th>SP6</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTE_1C</td>
<td>6382</td>
<td>189</td>
<td></td>
<td></td>
<td>33.8</td>
<td>65</td>
<td>98</td>
<td>39</td>
</tr>
<tr>
<td>LAP INT</td>
<td>19943</td>
<td>165</td>
<td></td>
<td></td>
<td>120.8</td>
<td>74</td>
<td>297</td>
<td>59</td>
</tr>
<tr>
<td>POISSON</td>
<td>1504</td>
<td>1.5</td>
<td></td>
<td></td>
<td>1002.6</td>
<td>0.5</td>
<td>3000</td>
<td>0.4</td>
</tr>
<tr>
<td>INTE_P</td>
<td>6311</td>
<td>189</td>
<td></td>
<td></td>
<td>33.4</td>
<td>100</td>
<td>63</td>
<td>106</td>
</tr>
<tr>
<td>LCAO INT</td>
<td>69037</td>
<td>372</td>
<td></td>
<td></td>
<td>185.6</td>
<td>171</td>
<td>403</td>
<td>167</td>
</tr>
<tr>
<td>HDIAGB</td>
<td>231096</td>
<td>545</td>
<td></td>
<td></td>
<td>424.0</td>
<td>121</td>
<td>1909</td>
<td>79</td>
</tr>
<tr>
<td>HDIAGC (12 E)</td>
<td>128039</td>
<td>1027</td>
<td></td>
<td></td>
<td>124.7</td>
<td>325</td>
<td>394</td>
<td>273</td>
</tr>
</tbody>
</table>

**Norcamphor ($C_8H_{10}O$) no symmetry**  
NDIM = 45408  
256 open channels  
IBM SP6

<table>
<thead>
<tr>
<th>NDIM</th>
<th>Open Channels</th>
<th>Configuration (1 E)</th>
<th>CPU</th>
<th>CPU</th>
<th>%ratio</th>
<th>CPU</th>
<th>%ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 CPU</td>
<td>128 CPU</td>
<td>HDIAGC</td>
<td>112.0</td>
<td>69.3</td>
<td>81%</td>
<td>50.5</td>
<td>56%</td>
</tr>
</tbody>
</table>
What can be done at the DFT level

- Cross sections $\sigma$ and asymmetry parameters $\beta$:
  oscillations and shape resonances: structures everywhere
- Dichroism in chiral molecules (dichroic parameter D)
- Photoionization from fixed in space molecules
- Non Dipolar Effects (ND parameters $\gamma$, $\delta$)
- Vibrationally resolved cross sections

**LARGE MOLECULES:** ~ $10^2$ atoms

~ 1 nm cluster
What is gained at the TDDFT level

- Correlation (response) effects due to the mixing of singly-excited configurations (channel mixing)
- Interchannel coupling effects
- Autoionization resonances due to discrete single excitations

What is missed

- Correlations due to multiple excitations
- Autoionizations due to doubly excited states
- Description of satellite states
Linear regime (1 photon)

\[ \frac{d\sigma_F}{dk} \rightarrow \langle \Psi_{Fk}(-) | D | \Psi_I \rangle = \langle \Psi_{Fk}(-) | \Phi_{DI} \rangle \]

projection of the “final wavepacket” or “prepared state” \( \Phi_{DI} \) onto a Field-Free final state (discrete or continuum) \( \Psi_{Fk}(-) \)

Can consider separately

1) Calculation of \( \Phi_{DI} \) \( (L^2) \)

2) Calculation of \( \Psi_{Fk}(-) \), equivalently \( \Psi_{FEj} \)
Multiphoton domain (FEL physics)

LOPT

\[ \Phi_{DI}^{(N_{ph})} = D \ (H-E_{N-1})^{-1} \ D \ (H-E_{N-2})^{-1} \ D \ldots \ D \ \Phi_I \]

\[ = D \ (H-E_{N-1})^{-1} \ \Phi_{DI}^{(N-1)} \quad E_m = E_I + m\omega \]

Strong Field Domain (Lasers and Ultrashort)

TDSE

\[ \Phi_{DI}(t) = U(t) \ \Phi_I \]

\[ i \ \partial / \partial t \ \Phi_{DI} = H(t) \ \Phi_{DI} \]

At least in a large domain, established paradigms
WAVEPACKETS - two main approaches

1. Diagonalize FF hamiltonian

\[ H_0 \Psi_i = E_i \Psi_i \]

\[
(H-E)^{-1} = \sum_i |\Psi_i> <\Psi_i| / (E_i - E)
\]

\[
i \frac{\partial}{\partial t} \Phi_{DI} = H(t) \Phi_{DI} \Rightarrow i \frac{\partial}{\partial t} c(t) = (E + V) c
\]

well conditioned, can truncate on energy criterion

2. Work in the primitive basis

\[
\Phi_{DI}^{(N)} = \sum_\mu \chi_\mu c_\mu^{(N)}
\]

\[
D_{\mu\nu} = <\chi_\mu|D|\chi_\nu>
\]

\[
\Phi_{DI}^{(N)} = D (H-E_{N-1})^{-1} \Phi_{DI}^{(N-1)} \Rightarrow (H-E_{N-1}) c^{(N)} = D c^{(N-1)}
\]

\[
i \frac{\partial}{\partial t} c^{(N)}(t) = H c^{(N)}
\]
The lowest order approach is employing an independent electron approach: choose a single particle hamiltonian, with an effective potential, and construct the full spectrum of the system as antisymmetrized product of single particle eigenstates

\[ H = h(1) + h(2) + \ldots + h(n) \]

\[ h\varphi_i = E_i \varphi_i \Rightarrow H\Phi_I = E_I \Phi_I \]

\[ \Phi_I = | \varphi_{i1} \varphi_{i2} \ldots \varphi_{in} \rangle \quad \quad E_I = E_{i1} + E_{i2} + \ldots + E_{in} \]

Then all equations and matrix elements reduce to 1-particle problems

Large problems become affordable
**LOPT**: first implementation at the DFT level (with D. Toffoli)

Diagonalize the DFT hamiltonian $h_{\text{KS}} \varphi_i = E_i \varphi_i$

The cross section is

$$\frac{d\sigma}{d\Omega} = 2\pi (2\pi \alpha \omega)^n |M_{f,i}^{(n)}|^2$$

with

$$M_{f,i}^{(2)} = \sum_m \frac{\langle \phi_f | D | \phi_m \rangle \langle \phi_m | D | \phi_i \rangle}{\omega_m - \omega_i - \omega}$$

In the two photon case

Angular momentum analysis gives total and differential cross sections

$$\frac{d\sigma^{(2)}}{d\hat{k}'} = \frac{\sigma^{(2)}}{4\pi} [1 + \sum L \beta_L P_L (\cos \theta)]$$

$$M_{lh}^{p\mu(-)}(\lambda_1, \lambda_2) = \sum_m \frac{\langle \phi_{lh}^{p\mu(-)} | \hat{\zeta} \lambda_1 \cdot \mathbf{r} | \phi_m \rangle \langle \phi_m | \hat{\zeta} \lambda_2 \cdot \mathbf{r} | \phi_i \rangle}{\omega_m - \omega_i - \omega}$$
FIG. 1. $\text{H}_2^+$ two-photon generalized cross section for parallel orientation at $R=2.0$ a.u.
FIG. 2. $H_2^+$ two-photon generalized cross section for orthogonal orientation at $R=2.0$ a.u.
$H_2^+$ two-photon generalized cross section for orthogonal relative orientation at $R=2.0$ a.u.
Ionization of molecules in intense laser field is a fundamental process that underlies most molecular strong field phenomena - HHG - ATI - MO imaging - Probing dynamics with attosecond resolution

Notably time resolved imaging of the electron clouds, imaging of the breaking and formation of chemical bonds.
A lot of information on the orbital nature is available through ionization of oriented molecules

- Coincidence with ions from fast molecular dissociation
- Alignment in laser fields: pump – probe
- Static fields
- Adsorbed molecules

With strong field ionization the angular dependence of ionization probability is supposed to map directly the structure of the HOMO
Strong field molecular ionization is generally addressed with simplified SAE models

- MO ADK (a pure tunnelling model)

- MO SFA (free electron in the field, several versions)

Many insights and useful results, sometimes gross quantitative differences

Only recently more quantitative and differential experimental results are becoming available

It is not expected that more than one active electron models become viable for large systems

But…. One-electron models can be treated exactly in a TDSE scheme
Given a single particle free field hamiltonian

\[ H^0 = \sum_i h^0(i) \]

the full field dependent hamiltonian is still single particle

\[ H(t) = \sum_i h^0(i) + \sum_i F(t) \cdot r(i) = \sum_i h(i, t) \]

\[ i \frac{\partial \Phi}{\partial t} = H(t) \Phi \quad \Rightarrow \quad i \frac{\partial \phi_k}{\partial t} = h(t) \phi_k \]

Two approaches

- SAE: only HOMO is propagated, all other orbitals (CORE) are frozen. HOMO is constrained to remain orthogonal to the core by the Pauli principle

- IAE: all orbitals are independently propagated. This is exact time propagation of the initial Slater determinant with the TD independent particle hamiltonian \( H(t) \). Because time evolution is unitary, orbitals remain orthonormal at all time, no Pauli principle violation.
SAE – TDSE (with A. Saenz, A. Castro)

- Propagation on the basis of $H_0$ eigenstates

$$H_0 \phi_k = E_k \phi_k$$

- Full diagonalization of the $H_0$ matrix

- Dipole matrix elements

$$d_{kl} = \langle \phi_k | d | \phi_l \rangle$$

- Gives access to strong field phenomena even for large systems

- Initial tests on $H_2$, benchmark with correlated calculations

- Current results on $N_2$, $O_2$, $F_2$, $CO_2$, $C_2H_2$, $H_2O$

$C_{60}$ will be feasible

Typical parameters, e.g. $CO_2$ (fixed geometry)

$$R_{max} = 200 \text{ a.u.} \quad \text{400 radial B-splines}$$

$\text{CO}_2$ SAE length gauge / IAE

![Graph showing angular distribution with labels $E_i$, $3\sigma_u$, $1\pi_g$, $1\pi_u$, $4\sigma_g$.]
CO$_2$ Field intensity dependence

![Normalized Ionization Yield vs Angle (degree)]

- Blue line with squares: $3 \times 10^{13}$ W/cm$^2$
- Orange line with diamonds: $7 \times 10^{13}$ W/cm$^2$
- Black line with triangles: $8 \times 10^{13}$ W/cm$^2$
- Red line with circles: $1 \times 10^{14}$ W/cm$^2$
- Red line with open squares: Exp., high intensity
- Blue line with open diamonds: Exp., low intensity
Experiment vs. MO-ADK

D. Pavcic et al., PRL 98 (2007) 243001
**MO-ADK**

**FIG. 1.** (Color online) Partial wave radial function of CO₂: (a) small-\(r\) region; (b) large-\(r\) region. The solid lines are from the present results, and dashed lines are calculated with GAMESS code. For clarity, in (b), the radial function for \(l=4\) (\(l=6\)) is divided by \(10^{2}\) (\(10^{4}\)).

**TABLE I.** The newly fitted \(C_l\) coefficients vs the old ones, for CO₂ \((m=1)\) and H\(^{+}\)\(_2\) \((m=0)\). Old data are from Refs. [8,18].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(I_p) (eV)</th>
<th>(R) (Å)</th>
<th>(C_{0m})</th>
<th>(C_{2m})</th>
<th>(C_{4m})</th>
<th>(C_{6m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ ((\pi_g))</td>
<td>13.769</td>
<td>1.163</td>
<td>1.27</td>
<td>0.188</td>
<td>0.014 ([18])</td>
<td></td>
</tr>
<tr>
<td>H(^{+})(_2) ((\sigma_g))</td>
<td>29.99</td>
<td>1.058</td>
<td>4.52</td>
<td>0.62</td>
<td>0.03</td>
<td>0.0         ([8])</td>
</tr>
</tbody>
</table>

**FIG. 2.** (Color online) The normalized alignment dependence of ionization rate of CO₂. The laser intensity is \(2 \times 10^{14}\) W/cm\(^2\). MO-ADK and SFA from [12].

---

Many accurate 1-particle approaches available

MO-ADK, long range tails

Ab-initio Tunnelling rates in a Static Field

Momentum space orbitals, separable potential approximations

Etc.
Strong Field and the Many-Body problem

In two electron system, full CI is basically exact, but how to extend to many electrons?

Single photon experience can be misleading! There mostly singly excited states + low lying doubly excited states, dominate the spectrum

Is Fermi sea concept still useful: can limit to multiple excitations within a quasidegenerate set, plus single excitations outside, eg nh-mv-1p CI space?

Or in real space, can you limit to only one electron beyond a certain radius? B-splines allow to implement it easily
Which configuration space does the system explore during the pulse, or how high in energy probes the spectrum of the free Hamiltonian?

Even in non-interacting system, dipole perturbation forces single excitations out of the HF GS, each new interaction couples to the next level of excitation. Moreover, \(1/r_{12}\) generates additional coupling.

Is anything to be learnt by propagating a non-interacting Hamiltonian? Use additional states so generated as basis for the full propagation?
The Next Step: go to HARD AB-INITIO

For small systems lot of detailed info is coming out

Basic Problem: generate an accurate many-particle spectrum of the Hamiltonian

\[ H\Psi = E\Psi \]

- Spectral basis for LOPT and TDSE
- Final continuum states
- Multielectron excitations
- Describe the physical spectrum explored by the system

Close-Coupling approach

Propagator approach  (ADC(2), V. Averbukh, CC-EOM)
- Bound state orbitals, multielectron bound state wfs → Quantum Chemistry, Gaussians
- Continuum orbitals → LCAO B-spline
- Mixed e-e integrals → expand in OCE B-splines, or Poisson
- Large scale parallel implementations, use state of the art HPC

Big computational Project: want to meet the challenge?
Join ITN CORINF → PhD positions available
\[ \langle \Phi_i^a | H-E0 | \Phi_j^b \rangle = \langle aj||ib \rangle = (ai | jb) - (ab | ij) \quad \text{RPA} \]

\[ = (ai | jb) + (ai | W | jb) \quad \text{TDDFT} \]

\[- (ab | ij) \to - c / R \quad \text{for large charge separation } R \]

\[(ai | W | jb) \to 0 \]

Here \( 3p \to v^* + v \to \epsilon l \)

\( i = 3p \quad a = v^* \quad j = v \quad b = \epsilon l \)

\[(v^* 3p | v \epsilon l) - (v^* \epsilon l | 3p v) \]

If \( 3p \to v^* \) is CT, only exchange is large, underestimated by TDDFT
\[ \Phi(t) = |\phi_1(t) \phi_2(t) \ldots \phi_n(t) \rangle \]
satisfies
\[ i \frac{\partial \Phi}{\partial t} = H(t) \Phi \]
provided
\[ i \frac{\partial \phi_k}{\partial t} = h(t) \phi_k \]
i.e. all electrons are propagated independently.
Since no change is allowed in the e-e interaction, the approximation will be better for strong fields, short times.

If only HOMO is significantly changed, similar results are expected from SAE and IAE. Actually, even in such conditions, SAE shows often large gauge dependence, while IAE stays strictly gauge invariant.