

Qbox calculations of dipole matrix elements

In a finite system, the calculation of dipole transition matrix elements between states i and j involves the evaluation of integrals

$$\langle \phi_i | r | \phi_j \rangle = \int_{\Omega} \phi_i(r) r \phi_j(r) dr$$

The dipole transition strength is expressed as

$$D_{ij}^2 = |\langle \phi_i | x | \phi_j \rangle|^2$$

Since the above integrals are not well defined in a periodic system, we use the following approximation[Res98], valid in the limit of a large unit cell (defined here for the x direction in a rectangular cell):

$$D_{ij}^2 \simeq \left| \frac{L_x}{2\pi i} \int_{\Omega} \phi_i(r) \exp\left(i \frac{2\pi}{L_x} x\right) \phi_j(r) dr \right|^2$$

This expression is invariant under changes of the origin of coordinates.

Qbox implementation

The integrals

$$\int_{\Omega} \phi_i(r) \exp\left(i \frac{2\pi}{L_x} x\right) \phi_j(r) dr$$

are evaluated using the `MLWFTTransform` class.

Verification

The dipole transition strength D_{ij}^2 of hydrogenic atoms can be evaluated exactly [Wal18]. The transition strengths were computed with Qbox using a single H^+ ion in a cubic unit cell and 14 empty states, i.e. 1s,2s,2p,3s,3p,3d.

	Exact (from [Wal18])	Qbox cell=120 bohr	Qbox cell=150 bohr
1s \rightarrow 2p	0.554932	0.554499	0.556074
1s \rightarrow 3p	0.08899	0.088514	0.088907
2s \rightarrow 2p	9	8.765552	8.848957
2s \rightarrow 3p	3.13103	2.890877	2.895562
3s \rightarrow 2p	0.293534 (*)	0.244428	0.260131
3d \rightarrow 2p	9.01736	8.6082 (**)	8.75611 (**)
3s \rightarrow 3p		47.5631	49.758265

(*) The value of $D^2(2p \rightarrow 3s)$ 0.88060 in [Wal18] which includes a sum over m . Other values in [Wal18] are for one m only. The value for a single m is $0.88060/3 = 0.293534$.

(**) computed value is $(1/5) * \sum(m, m') D^2(m, m')$.

Appendix

Qbox script for the calculation of the hydrogen dipole transition strengths

```
set cell 120 0 0 0 120 0 0 0 120
species hydrogen H_ONCV_PBE-1.2.xml
atom H1 hydrogen 0 0 0
set ecut 100
set net_charge 1
set nempty 14
set wf_dyn JD
randomize_wf
run 0 10 10
# add small charge in 1s state to trigger calculation of spectrum
set occ 1 1.e-8
spectrum sp.dat
save h.xml
```

The transition strengths D_{ij}^2 are evaluated by the `spectrum` command.

If the wave function has already been computed (including some empty states) and is saved in a file named `file.xml`, the following script can be used:

```
load file.xml
spectrum sp.dat
```

Dipole matrix elements are printed with the following format

```
<dipole_matrix_elements spin="0">
  <dipole i="1" j="2">    10.131958    0.546053 </dipole>
  <dipole i="1" j="3">    10.131958    0.546053 </dipole>
  <dipole i="1" j="4">    10.131958    0.546053 </dipole>
  <dipole i="1" j="5">    10.141309    0.007940 </dipole>
  <dipole i="1" j="6">    11.978679    0.000963 </dipole>
  <dipole i="1" j="7">    11.985567    0.083425 </dipole>
  ...
```

where the first number is the energy difference in eV and the second number is the dipole transition

strength $D_{ij}^2 = cx*cx + sx*sx + cy*cy + sy*sy + cz*cz$, where $cx = \frac{L_x}{2\pi} \langle \phi_i | \cos\left(\frac{2\pi}{L_x}x\right) | \phi_j \rangle$ and

similar definitions hold for sx , etc. The dipole transition strength

Example output:

```
<eigenvalues spin="0" kpoint="0 0 0" weight="1" n="14">
  -12.261    -2.129    -2.129    -2.129    -2.1196
  -0.28225   -0.27536   -0.27536   -0.27536   -0.26241
  -0.26241   -0.25996   -0.25996   -0.25996
</eigenvalues>
```

```

<dipole_matrix_elements spin="0">
  <dipole i="1" j="2">    10.131958    0.546053 </dipole>
  <dipole i="1" j="3">    10.131958    0.546053 </dipole>
  <dipole i="1" j="4">    10.131958    0.546053 </dipole>
  <dipole i="1" j="5">    10.141309    0.007940 </dipole>
  <dipole i="1" j="6">    11.978679    0.000963 </dipole>
  <dipole i="1" j="7">    11.985567    0.083425 </dipole>
  <dipole i="1" j="8">    11.985567    0.083425 </dipole>
  <dipole i="1" j="9">    11.985567    0.083425 </dipole>
  <dipole i="1" j="10">   11.998514    0.001005 </dipole>
  <dipole i="1" j="11">   11.998514    0.001005 </dipole>
  <dipole i="1" j="12">   12.000970    0.000000 </dipole>
  <dipole i="1" j="13">   12.000970    0.000000 </dipole>
  <dipole i="1" j="14">   12.000970    0.000000 </dipole>
</dipole_matrix_elements>

```

References

- [1] R. Resta, *Quantum-Mechanical Position Operator in Extended Systems*, Phys. Rev. Lett. 80, 1800 (1998).
- [2] J. T. M. Walraven, *Atomic Physics Lectures*, University of Amsterdam (2018).
https://staff.fnwi.uva.nl/j.t.m.walraven/walraven/Publications_files/2019-AtomicPhysics.pdf