# Supporting Information for: Large-scale cubic-scaling RI-RPA correlation energy calculations

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# 1 RPA correlation energy with resolution of the identity

In this section, we derive Eq. (21) from the main manuscript. We start from Eq. (16) in the main manuscript,

$$E_{\mathrm{c}}^{\mathrm{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \, \mathrm{Tr}\left[\ln\left(1 - \chi(i\omega)v\right) + \chi(i\omega)v\right] . \tag{1}$$

The function $\ln(1-x)+x$ in the integrand of Eq. (1) can be evaluated by its Taylor series

$$\ln(1-x) + x = -\sum_{n=2}^{\infty} x^n/n \tag{2}$$

as

$$E_{\mathrm{c}}^{\mathrm{RPA}} = -\frac{1}{2\pi} \int_0^\infty d\omega \sum_{n=2}^{\infty} \frac{\mathrm{Tr}\left[\chi(i\omega)v\right]^n}{n} \tag{3}$$

The trace of the $n$th power of $\chi(i\omega)v$ is given by

$$\begin{aligned} \mathrm{Tr}[\chi(i\omega)v]^n = \int & d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_{2n} \chi(\mathbf{r}_1, \mathbf{r}_2, i\omega) v(\mathbf{r}_2, \mathbf{r}_3) \\ & \times \chi(\mathbf{r}_3, \mathbf{r}_4, i\omega) v(\mathbf{r}_4, \mathbf{r}_5) \ldots \chi(\mathbf{r}_{2n-1}, \mathbf{r}_{2n}, i\omega) v(\mathbf{r}_{2n}, \mathbf{r}_1) . \end{aligned} \tag{4}$$

Then, the RPA correlation energy from Eq. (1) reads

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{RPA}} = -\frac{1}{2\pi} \int_0^\infty d\omega \sum_{n=2}^{\infty} \frac{1}{n} \int & d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_{2n} \chi(\mathbf{r}_1, \mathbf{r}_2, i\omega) v(\mathbf{r}_2, \mathbf{r}_3) \\ & \times \chi(\mathbf{r}_3, \mathbf{r}_4, i\omega) v(\mathbf{r}_4, \mathbf{r}_5) \ldots \chi(\mathbf{r}_{2n-1}, \mathbf{r}_{2n}, i\omega) v(\mathbf{r}_{2n}, \mathbf{r}_1) . \end{aligned} \tag{5}$$

With the definition of the density response function from Eq. (17) from the main manuscript,

$$\chi(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{virt}} \psi_a(\mathbf{r}')\psi_i(\mathbf{r}')\psi_i(\mathbf{r})\psi_a(\mathbf{r}) \, \frac{\varepsilon_i - \varepsilon_a}{\omega^2 + (\varepsilon_i - \varepsilon_a)^2} ,$$

we obtain with Eq. (5) from above:

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{1}{n}\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_{2n} \\
\times 2\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{virt}} \psi_a(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\psi_a(\mathbf{r}_2)\,\frac{\varepsilon_i-\varepsilon_a}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}\,v(\mathbf{r}_2,\mathbf{r}_3) \\
\times 2\sum_{j}^{\mathrm{occ}}\sum_{b}^{\mathrm{virt}} \psi_b(\mathbf{r}_3)\psi_j(\mathbf{r}_3)\psi_j(\mathbf{r}_4)\psi_b(\mathbf{r}_4)\,\frac{\varepsilon_j-\varepsilon_b}{\omega^2+(\varepsilon_j-\varepsilon_b)^2}v(\mathbf{r}_4,\mathbf{r}_5) \\
\times \ldots \times 2\sum_{k}^{\mathrm{occ}}\sum_{c}^{\mathrm{virt}} \psi_c(\mathbf{r}_{2n-1})\psi_k(\mathbf{r}_{2n-1})\psi_k(\mathbf{r}_{2n})\psi_c(\mathbf{r}_{2n})\,\frac{\varepsilon_k-\varepsilon_c}{\omega^2+(\varepsilon_k-\varepsilon_c)^2}v(\mathbf{r}_{2n},\mathbf{r}_1)\,.
\end{aligned}
\tag{6}
$$

With the definition of the four-center electron repulsion integrals from Eq. (2) of the main manuscript,

$$
(ia|jb) = \int d\mathbf{r}d\mathbf{r}'\,\psi_i(\mathbf{r}')\psi_a(\mathbf{r}')\psi_j(\mathbf{r})\psi_b(\mathbf{r})v(\mathbf{r},\mathbf{r}')\,,
$$

we obtain from Eq. (6)

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{1}{n}\sum_{i,j,k,\ldots}^{\mathrm{occ}}\sum_{a,b,c,\ldots}^{\mathrm{virt}} \frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}\,(ia|jb)\,\frac{2(\varepsilon_j-\varepsilon_b)}{\omega^2+(\varepsilon_j-\varepsilon_b)^2}(jb|\ldots \\
\ldots|kc)\,\frac{2(\varepsilon_k-\varepsilon_c)}{\omega^2+(\varepsilon_k-\varepsilon_c)^2}(kc|ia)\,.
\end{aligned}
\tag{7}
$$

We insert the resolution of the identity (RI) from Eq. (9) in the main manuscript, $(ia|jb) = \sum_P B_P^{ia} B_P^{jb}$, into Eq. (7) and obtain

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{1}{n}\sum_{i,j,k,\ldots}^{\mathrm{occ}}\sum_{a,b,c,\ldots}^{\mathrm{virt}}\sum_{P,Q,R,T,\ldots} B_T^{ia}\frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}B_P^{ia}B_P^{jb}\,\frac{2(\varepsilon_j-\varepsilon_b)}{\omega^2+(\varepsilon_j-\varepsilon_b)^2}B_Q^{jb} \\
\ldots B_R^{kc}\,\frac{2(\varepsilon_k-\varepsilon_c)}{\omega^2+(\varepsilon_k-\varepsilon_c)^2}B_T^{kc}\,.
\end{aligned}
\tag{8}
$$

We employ the definition of $\mathbf{Q}(w)$ from Eq. (22) of the main manuscript,

$$
Q_{PQ}(\omega) = 2\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{virt}} B_P^{ia}\,\frac{\varepsilon_a-\varepsilon_i}{\omega^2+(\varepsilon_a-\varepsilon_i)^2}\,B_Q^{ia}\,,
$$

and Eq. (8) simplifies to

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} &= -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{(-1)^n}{n}\sum_{P,Q,R,T,\ldots} Q_{TP}(\omega)Q_{PQ}(\omega)\ldots Q_{RT}(\omega) \\
&= -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{(-1)^n}{n}\,\mathrm{Tr}\left[\mathbf{Q}^n(\omega)\right] \\
&= -\frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\sum_{n=2}^{\infty}\frac{(-1)^n}{n}\,\mathbf{Q}^n(\omega)\right] \\
&= \frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\ln(\mathbf{1}+\mathbf{Q}(\omega))-\mathbf{Q}(\omega)\right]\,. \qquad (9)
\end{aligned}
$$

The equation above is Eq. (21) from the main manuscript which was supposed to be derived.

# 2 Exemplary input file

```
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME      BASIS_RI_cc-TZ
    POTENTIAL_FILE_NAME      POTENTIAL
    WFN_RESTART_FILE_NAME    H2O-1024-RI-RPA-TZ-RESTART.wfn
    &MGRID
     CUTOFF      800
     REL_CUTOFF   50
    &END MGRID
    &QS
      EPS_DEFAULT 1.0E-12
    &END QS
    &SCF
      SCF_GUESS  RESTART
      EPS_SCF    1.0E-6
      MAX_SCF    20
      &OT
        MINIMIZER       CG
        PRECONDITIONER  FULL_ALL
      &END
      &OUTER_SCF
        EPS_SCF  1.0E-6
        MAX_SCF  20
      &END
      &PRINT
        &RESTART OFF
        &END
      &END
    &END SCF
    &XC
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &WF_CORRELATION
        METHOD  RI_RPA_GPW
        RI OVERLAP
        ERI_METHOD MME
        &RI_RPA
          MINIMAX_QUADRATURE
          RPA_NUM_QUAD_POINTS    15
          IM_TIME
          &IM_TIME
            ! memory_cut is the factor of memory reduction
            MEMORY_CUT 14
            ! number of processes for the p group
            GROUP_SIZE_P 1
            ! number of processes for the q group
            GROUP_SIZE_3c 36
            EPS_FILTER_IM_TIME 1.0E-8
          &END
        &END
        &WFC_GPW
          EPS_FILTER  3.0E-6
          ! filter for computing the 3-center matrix elements
          EPS_GRID    3.0E-4
          OSO TRUE
        &END
        NUMBER_PROC 4
      &END
    &END XC
  &END DFT
    ⋮
    ⋮
  &SUBSYS
    &CELL
      ABC 9.8528 9.8528 9.8528
      MULTIPLE_UNIT_CELL  32  1  1
    &END CELL
    &TOPOLOGY
       COORD_FILE_NAME   H2O-32.xyz
       COORD_FILE_FORMAT cp2k
      MULTIPLE_UNIT_CELL  32  1  1
    &END TOPOLOGY
    &KIND H
      BASIS_SET         cc-TZ
      RI_AUX_BASIS_SET  RI-cc-TZ
      POTENTIAL         GTH-PBE-q1
    &END KIND
    &KIND O
      BASIS_SET         cc-TZ
      RI_AUX_BASIS_SET  RI-cc-TZ
      POTENTIAL         GTH-PBE-q6
    &END KIND
  &END SUBSYS
&END FORCE_EVAL
&GLOBAL
  PROJECT     H2O-32-RI-RPA-TZ
  RUN_TYPE    ENERGY
  PRINT_LEVEL MEDIUM
  EXTENDED_FFT_LENGTHS
&END GLOBAL
```

Figure 1: Input example for computing the RPA correlation energy of 1024 water molecules on 256 nodes with 36 CRAY-XC40 cores per node on the supercomputer Piz Dora in august 2016. The following files are needed: BASIS_RI_cc-TZ, containing basis parameters (retrievable from the CP2K release); POTENTIAL, containing the pseudopotential parameters (retrievable from the CP2K release) and struc.xyz, coordinate file with the geometry which is contained in this supporting information.

# 3 Geometry of the basic 32 water cell

```
O       0.228972       5.884026       6.532308
H       0.554129       2.982634       8.082024
H       0.939475       5.243834       6.571945
O       0.856426       2.075964       5.010625
H       0.515723       6.520548       5.877445
H       0.350256       2.874437       4.860741
O       0.846293       5.595877       3.820630
H       0.427645       4.908936       3.301903
H       0.837635       8.186808       8.987268
O       1.251703       2.406261       7.769908
H       1.762019       9.820429       5.528454
H       1.771257       2.954779       7.182181
O       1.596302       6.920128       0.656695
H       1.776389       7.463264       1.424030
H       1.999705       2.060411       1.927796
O       1.453702       1.402538       2.358278
H       1.824184       0.564565       2.081195
H       1.160987       1.818023       4.140602
O       1.337625       8.580920       8.272484
H       1.637363       5.184910       4.169264
H       1.872601       7.864672       7.930401
O       2.280398       9.146539       5.088696
H       2.112148       6.126321       0.798136
H       2.720238       9.146974       3.273164
O       2.957518       3.771868       1.877387
H       3.095987       9.107088       5.588186
H       3.754249       3.824017       1.349436
O       2.802896       8.690383       2.435952
H       3.010580       4.524142       2.466878
H       3.576065       9.078451       2.026264
O       2.766709       0.881503       9.544263
H       3.260797       5.243390       5.962382
H       3.347848       3.732214       5.988196
O       2.733023       4.452756       5.850203
H       2.415851       1.576460       8.987338
H       2.276957       0.099537       9.289499
O       3.665373       6.210561       3.158420
H       3.273115       7.061666       2.963521
H       4.467366       9.971162       0.219851
O       3.371648       6.925594       7.476036
H       3.878372       7.435003       6.843607
H       3.884673       6.966316       8.283117
O       4.962043       4.134437       0.173376
H       5.758685      10.102795       0.998994
H       5.248010       5.018415       0.403676
O       4.600039       9.254314       6.575944
H       4.749903       4.186003      -0.758595
H       4.566850       6.413356       3.408312
   ⋮
```

```
   ⋮
O       5.090422       9.467016       0.743177
H       5.768804       2.638450       0.375264
H       5.328688       9.073059       5.982269
O       5.287920       3.270653       6.155080
H       5.007063       9.672150       7.334875
H       5.918240       3.116802       5.451335
O       5.225237       6.959594       9.582991
H       5.355924       2.495093       6.711958
H       5.071858       7.687254      10.185667
O       6.330888       7.363471       3.747750
H       6.652693       7.917443       3.036562
H       6.711966       7.743594       4.539279
O       6.536550       1.146790       7.609732
H       6.576029       1.537017       8.482885
H       6.106394       7.112302       9.241707
O       6.386036       1.918950       0.242690
H       7.995317       4.290074       3.474723
H       7.221823       2.257514       0.563730
O       7.763819       8.349367       9.279457
H       7.430334       0.849764       7.438978
H       7.751955       8.745180      10.150905
O       7.256289       8.493641       5.772041
H       7.829208       9.092212       8.679343
H       7.886607       7.941321       6.234506
O       8.280798       3.837153       5.799282
H       7.793855       9.141028       5.315813
H       8.556008       6.860063      -0.294256
O       8.878250       2.025797       1.664102
H       8.312540       3.218330       6.528858
H       8.508855       4.680699       6.189990
O       8.509982       4.430362       2.679946
H       8.799060       2.876412       2.095861
H       8.046808       5.126383       2.213838
O       8.054437       9.221335       1.991376
H       8.314696      10.115534       2.212519
H       8.687134       8.667252       2.448452
O       9.785620       8.164617       3.657879
H       9.971698       7.227076       3.709104
H       9.085561       4.493058       9.031660
O       9.123223       3.549232       8.876721
H       9.215391       3.166305       9.749133
H       9.505360       1.161677       6.701213
O       9.160372       0.285100       6.871004
H       9.920117      -0.219794       7.161006
H       9.742249       1.704975       1.922581
O       9.023431       6.119654       0.092451
H       9.852960       6.490366       0.393593
H      10.647901       8.579244       3.629806
```

Figure 2: Coordinates of the basis cell containing 32 water molecules in the xyz format.