



Extension of LCAO to excited states: Details

Application to excitation spectra within TDDFT linear response.

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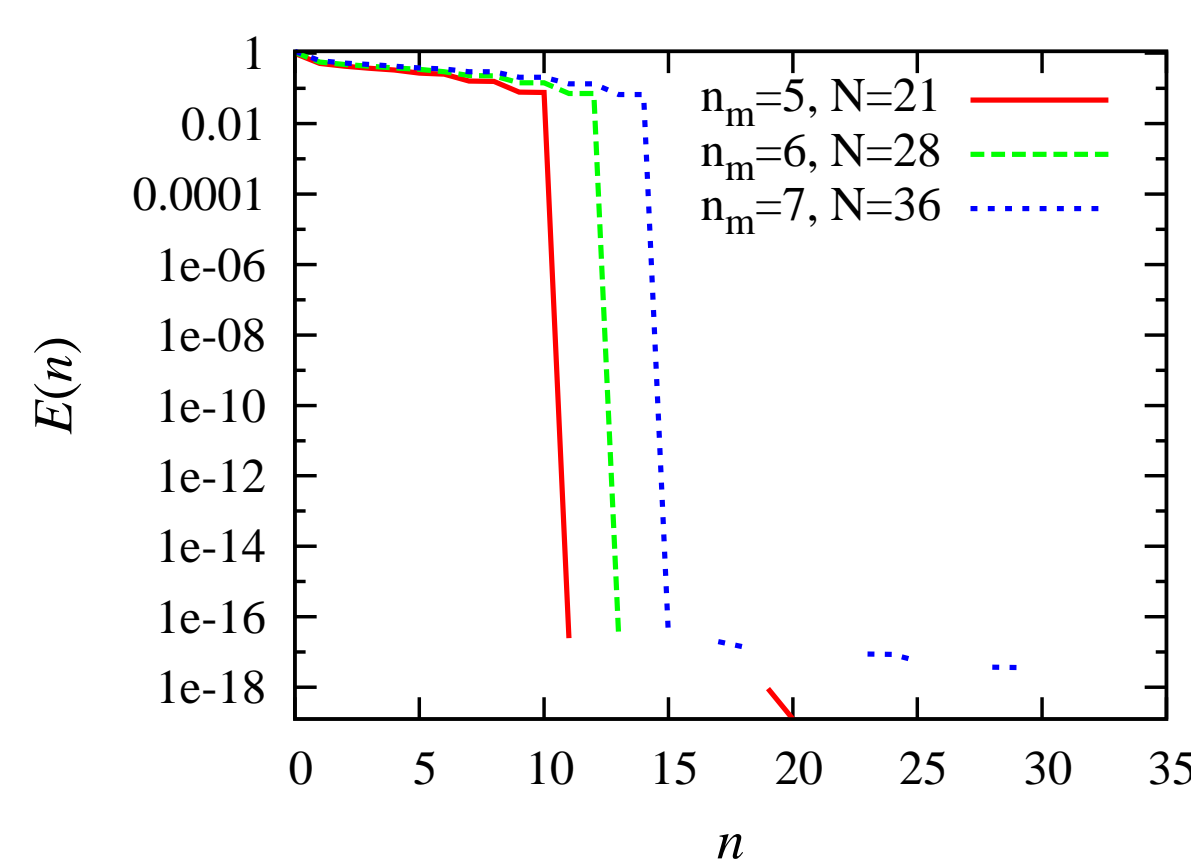
Extension of LCAO: guiding idea

- LCAO expansion of an electron annihilation operator reads: $\psi(\mathbf{r}, t) = \sum_p f^p(\mathbf{r}) c_p(t)$.
- Density appearing in the theory of excited states reads: $n(\mathbf{r}, t) = \psi^\dagger(\mathbf{r}, t) \psi(\mathbf{r}, t) = \sum_{pq} f^p(\mathbf{r}) f^q(\mathbf{r}) c_p^\dagger(t) c_q(t)$.
- Products $f^p(\mathbf{r}) f^q(\mathbf{r})$ are known to be linearly dependent. Therefore it is useful to expand them in a small set of basis functions $F^\mu(\mathbf{r})$

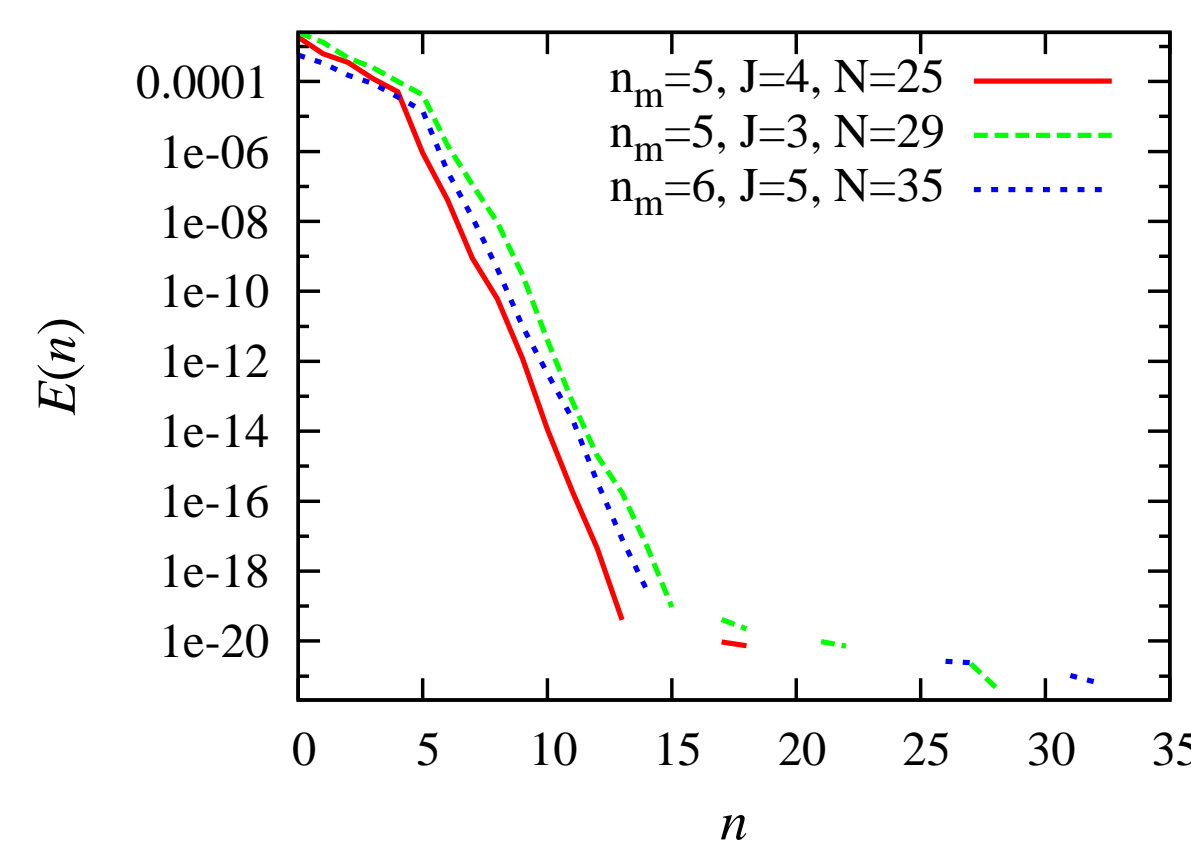
$$f^p(\mathbf{r}) f^q(\mathbf{r}) = \sum_\mu V_\mu^{pq} F^\mu(\mathbf{r}).$$

Construction of product basis $\{F^\mu(\mathbf{r})\}$

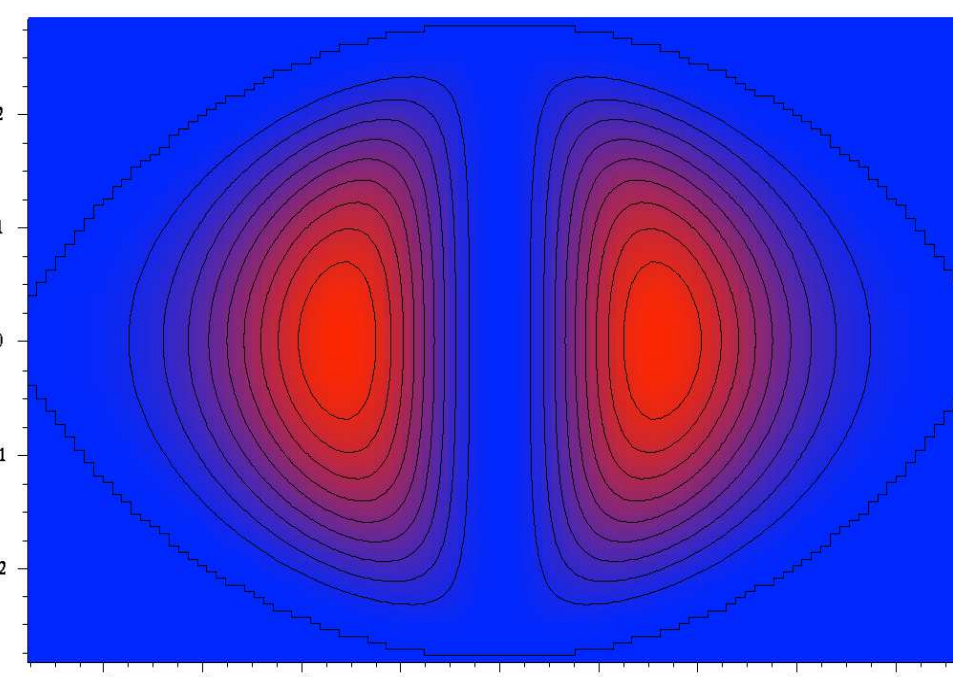
- Linear dependence of products of eigenstates: example of harmonic oscillator** $\psi_n(x) \sim e^{-x^2/2} H_n(x)$, $n = 0 \dots N$.
 $\{H_m(x) \cdot H_n(x) e^{-x^2}\}_{m,n=0 \dots N} \Rightarrow \{H_n(\sqrt{2}x) e^{-x^2}\}_{n=0 \dots 2N}$. Only $2N + 1$ out of $(N + 1)(N + 2)/2$ products are linearly independent.
- Diagonalise **metric of products** $\mathbf{g} = \int d^3r F_{ab}(\mathbf{r}) F_{cd}(\mathbf{r})$ [1], $\mathbf{g} \mathbf{X}^E = \mathbf{E} \mathbf{X}^E$; Define **dominant products** $F^E(\mathbf{r}) = \sum_{ab} \mathbf{X}_{ab}^E F_{ab}(\mathbf{r})$ [2]
- Eigenvalues of metric have a sharp dropoff in case of harmonic oscillator and a smooth behavior for Coulomb problem



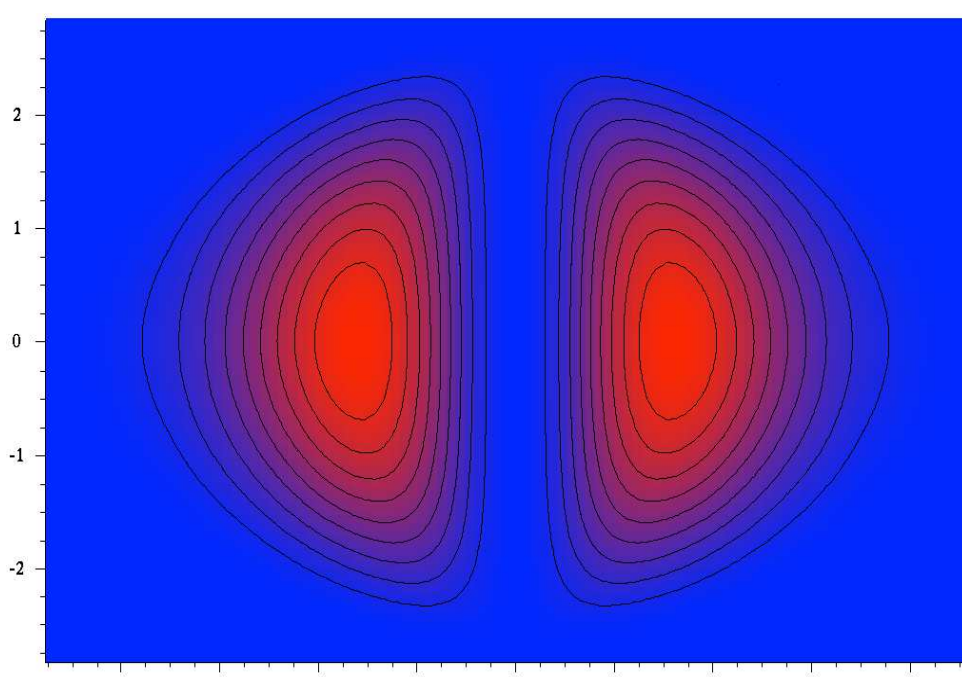
Harmonic oscillator



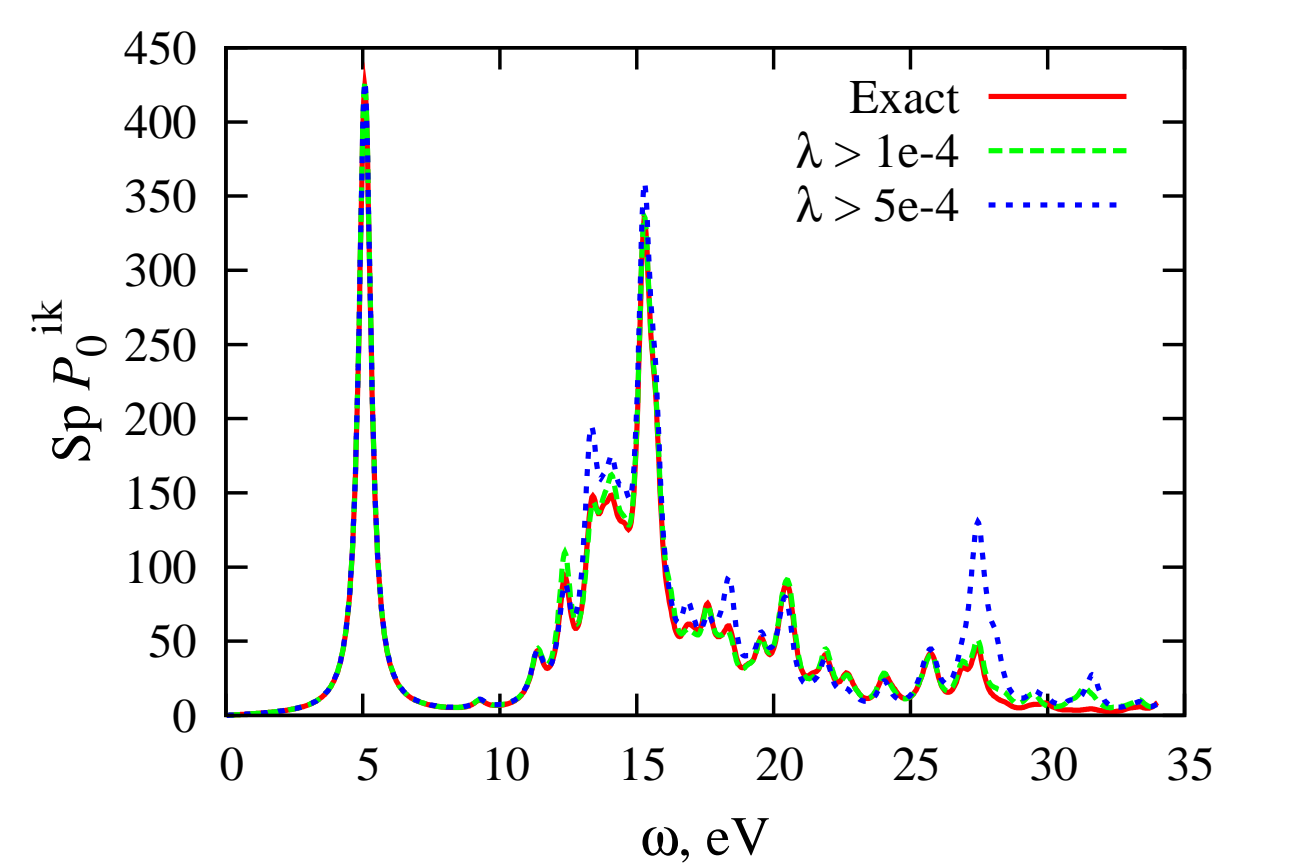
Coulomb oscillator



A bilocal product: exact



Expanded in dominant products



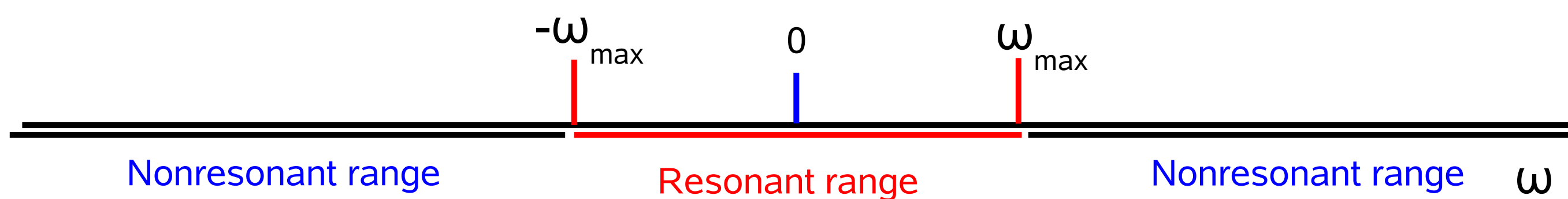
First test: free polarizability of benzene

- Spectrum of eigenvalues in the tail satisfies $\frac{dn}{dE} = -\frac{1}{E}$; it resembles the $1/f$ noise in semiconductors.

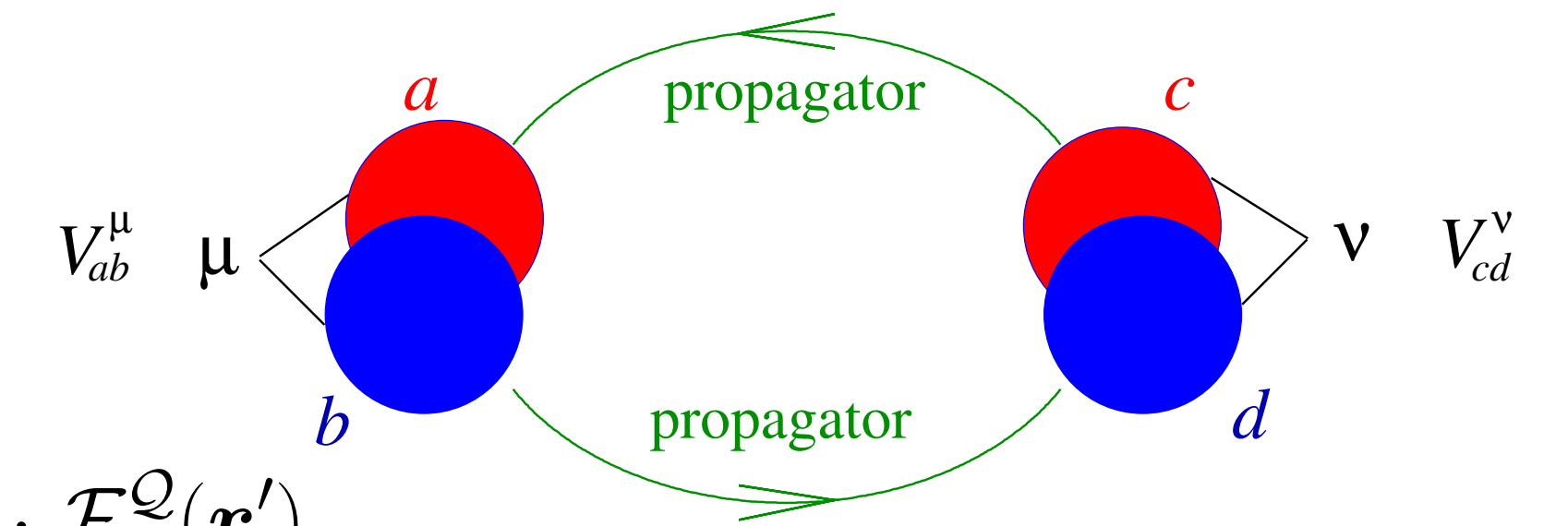
Fast free response in product basis

- Traditional expression for free-response $\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{EF} (n_F - n_E) \frac{\psi_E(\mathbf{r}) \psi_F(\mathbf{r}) \psi_E(\mathbf{r}') \psi_F(\mathbf{r}')}{\omega - (E - F) + i\epsilon}$
- Free response in time domain $\chi_0(\mathbf{r}t, \mathbf{r}'0) = -i \langle \psi_0 | T[\hat{n}(\mathbf{r}t), \hat{n}(\mathbf{r}'0)] | \psi_0 \rangle = -i \sum_{PQ} \mathcal{F}^P(\mathbf{r}) \text{Tr}(\mathbf{G}_{da}(t) \mathcal{V}_{ab}^P \mathbf{G}_{bc}(-t) \mathcal{V}_{cd}^Q) \cdot \mathcal{F}^Q(\mathbf{r}')$
- Green's function method "decouples" the sum over eigenstates \sum_{EF} and results in an $O(N^2 N_\omega)$ algorithm.
- Pitfall: calculation of $\chi_0(\omega)$ in the frequency range $(-\omega_{max} \dots \omega_{max})$ with a Green's function in $(-\omega_{max} \dots \omega_{max})$ gives wrong real part of $\chi_0(\omega)$**
- Way out: Kramers-Kronig spectral representation for free response** $\chi_0(\omega) = \int_{-\infty}^{+\infty} d\lambda \frac{a(\lambda) + b(\lambda)}{\omega - \lambda + i\epsilon}$ separate into **resonant** and **non-resonant** parts [3]

$$\chi_0(\omega) = \int_{-\infty}^{-\omega_{max}} d\lambda \frac{b(\lambda)}{\omega - \lambda + i\epsilon} + \int_{-\omega_{max}}^{+\omega_{max}} d\lambda \frac{a(\lambda)}{\omega - \lambda + i\epsilon} + \int_{\omega_{max}}^{+\infty} d\lambda \frac{b(\lambda)}{\omega - \lambda + i\epsilon}$$

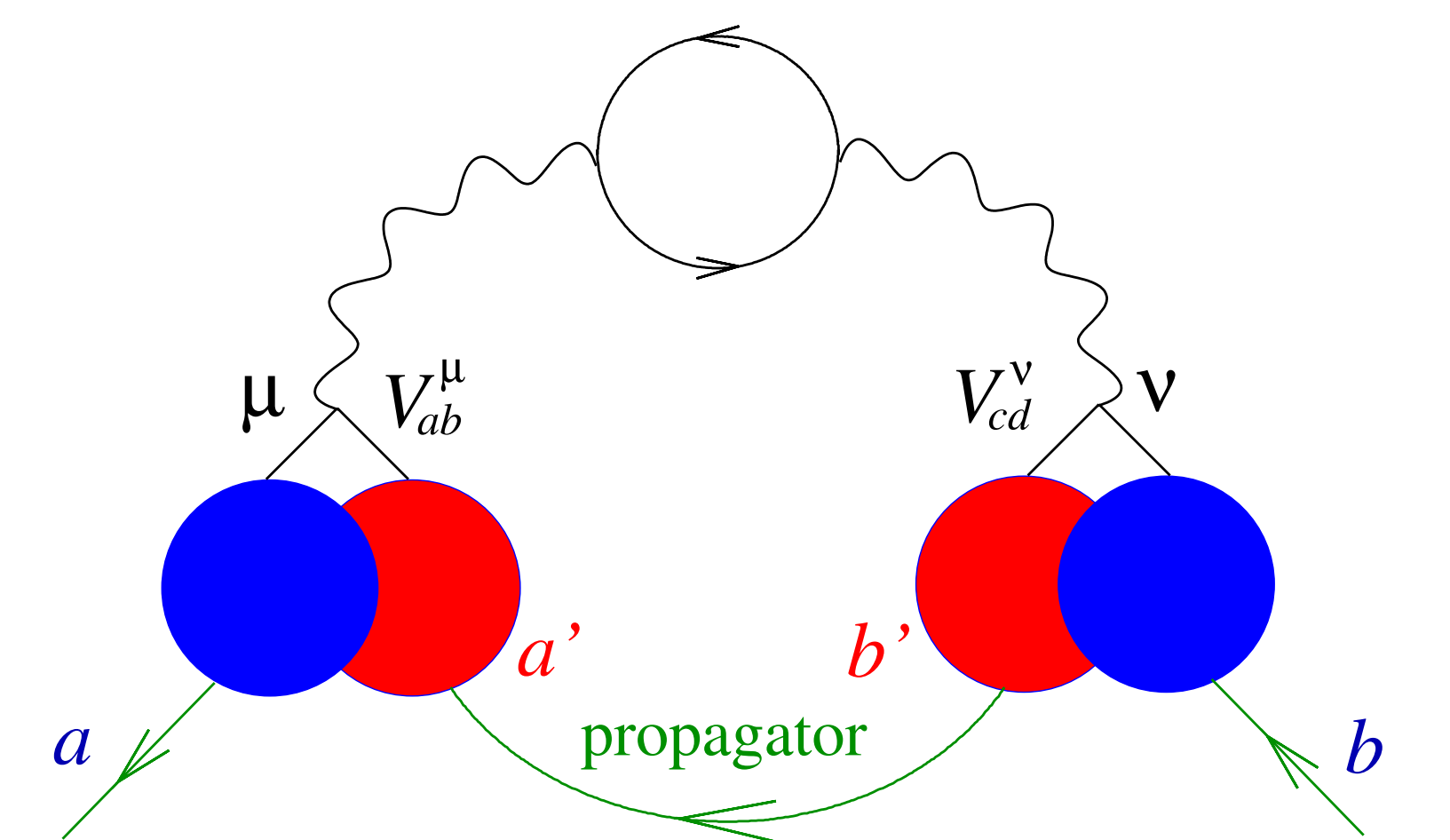


- Bosonic spectral function $a(\lambda)$ is a convolution of electronic spectral functions $\rho_{ab}(\epsilon) = \sum_E X_a^E X_b^E \delta(E - \epsilon)$: $a(\lambda) = \text{Tr}(\mathcal{V}_{ab}^P \mathcal{V}_{cd}^Q) \rho_{ac}(\epsilon) \otimes \rho_{bd}(\epsilon)$.
- FFT is used for convolutions [3]. Spectral function method remains exact up to discretisation of spectral functions.



GW within the basis of dominant products

- One-particle Green's function obeys: $(E - H_0(\mathbf{r})) G(\mathbf{r}, \mathbf{r}'; E) - \int d\mathbf{r}'' \Sigma(\mathbf{r}, \mathbf{r}'', E) G(\mathbf{r}'', \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}')$
- Self-energy operator in one-shot GW: $\Sigma(\mathbf{r}, \mathbf{r}', E) = \frac{i}{2\pi} \int d\omega' G_0(\mathbf{r}, \mathbf{r}'; E + \omega') W_0(\mathbf{r}, \mathbf{r}'; \omega')$
- Screened Coulomb interaction: $W_0(\mathbf{r}, \mathbf{r}'; \omega') = \int d\mathbf{r}'' \left(\delta(\mathbf{r} - \mathbf{r}'') - \int d\mathbf{s} V_H(\mathbf{r} - \mathbf{s}) \chi_0(\mathbf{s}, \mathbf{r}'', \omega') \right)^{-1} V_H(\mathbf{r}'' - \mathbf{r}')$.
- In our basis: screened Coulomb interaction $W_0(\omega) = (I - V_H \chi^0(\omega))^{-1} V_H$; V_H is bare Coulomb interaction.
- Self-energy operator $\Sigma_{rs} = i \sum_{pq\mu\nu} G_{pq}^0 \otimes V_\mu^{pr} W_0^{\mu\nu} V_\nu^{qs}$.
- Improved quasiparticle energies are expected.



References

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- [2] Foerster D., J. Chem. Phys. **128** 034108 (2008)
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- [4] Koch E. E. and Otto A., Chem. Phys. Lett. **12** 476 (1972)
- [5] Brown R., IPREM, unpublished (2008)