Supplemental material to the manuscript
"Bond breaking and bond making: how electron correlation is captured in many-body and density-functional theory"

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As discussed in the main text, the ground-state total-energy expression for an interacting electron system can be obtained using the adiabatic-connection (AC) technique

$$E = T_{\rm s} + \int d\mathbf{r}\, n(\mathbf{r})(v_{\rm ext}(\mathbf{r}) + \frac{1}{2}v_{\rm H}(\mathbf{r})) + \int_0^1 \frac{d\lambda}{2\lambda}{\rm Tr}\,[\Sigma_\lambda G_\lambda]\,, \tag{1}$$

where

$${\rm Tr}\,[AB] = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{i\omega\eta}\int d\mathbf{r}d\mathbf{r}'\, A(\mathbf{r},\mathbf{r}',i\omega)B(\mathbf{r}',\mathbf{r},i\omega)\,, \tag{2}$$

$T_{\rm s}$ is the kinetic energy of the Kohn-Sham (KS) independent-particle system, $v_{\rm ext}(\mathbf{r})$ the external potential, $v_{\rm H}(\mathbf{r}) = \int d\mathbf{r}'n(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')$ the classical Hartree potential, and $n(\mathbf{r})$ is the electron density which is fixed at its physical value along the AC path. Here G_λ and Σ_λ are respectively the interacting single-particle Green function and the self-energy for the "intermediate" system where the electrons interact with scaled Coulomb interaction $v_\lambda(\mathbf{r}-\mathbf{r}') = \lambda v(\mathbf{r}-\mathbf{r}') = \lambda/|\mathbf{r}-\mathbf{r}'|$. Please note that, in contrast with the main paper, the "Tr" operator in Eq. (1) and below also includes the frequency integration for notational simplicity.

The key question now is how to integrate the coupling constant λ out. To this end, it is customary to introduce the so-called Φ functional, defined as:

$$\Phi_\lambda[G_\lambda] = \sum_{n=1}^{\infty}\frac{1}{2n}{\rm Tr}\left[\Sigma_\lambda^{(n)}[G_\lambda]G_\lambda\right]\,, \tag{3}$$

where $\Sigma_\lambda^{(n)}$ is the sum of the n-th order terms of the self-energy expanded in terms of the (scaled) Coulomb interaction. In terms of Feynman diagrams, $\Sigma_\lambda^{(n)}$ only includes graphs that contain n explicit Coulomb lines. It should be kept in mind that $\Sigma_\lambda^{(n)}$ depends on λ in two ways: explicitly via the scaled Coulomb lines (there are n of them!) and implicitly via G_λ (there are $2n+1$ of them!). The multiplication of G_λ with $\Sigma_\lambda^{(n)}$ in ${\rm Tr}\left[\Sigma_\lambda^{(n)}G_\lambda\right]$ closes the self-energy diagrams, yielding the n-th order Φ-digrams which contain $2n$ Green-function lines. A key property of Φ_λ is therefore

$$\delta\Phi_\lambda/\delta G_\lambda = \sum_{n=1}^{\infty}\Sigma_\lambda^{(n)} = \Sigma_\lambda\,. \tag{4}$$

The derivative of Φ_λ with respect to λ is given by

$$\begin{aligned}\frac{d\Phi_\lambda}{d\lambda} &= \sum_{n=1}^{\infty}\frac{1}{2n}{\rm Tr}\left[\frac{n}{\lambda}\Sigma_\lambda^{(n)}G_\lambda\right] + {\rm Tr}\left[\frac{\delta\Phi_\lambda}{\delta G_\lambda}\frac{dG_\lambda}{d\lambda}\right]\\ &= \frac{1}{2\lambda}{\rm Tr}\,[\Sigma_\lambda G_\lambda] + {\rm Tr}\left[\Sigma_\lambda\frac{dG_\lambda}{d\lambda}\right]\,.\end{aligned} \tag{5}$$

Making use of Eq. (5), Eq. (1) becomes

$$\begin{aligned}E =& T_{\rm s} + \int d\mathbf{r}\, n(\mathbf{r})v_{\rm ext}(\mathbf{r}) + E_{\rm H}[G] +\\ &\int_0^1 d\lambda\left\{\frac{d\Phi_\lambda}{d\lambda} - {\rm Tr}\left[\Sigma_\lambda\frac{dG_\lambda}{d\lambda}\right]\right\}\\ =& T_{\rm s} + \int d\mathbf{r}\, n(\mathbf{r})v_{\rm ext}(\mathbf{r}) + E_{\rm H} + \Phi_{\lambda=1}[G_{\lambda=1}]\\ &- {\rm Tr}\,[\Sigma_{\lambda=1}G_{\lambda=1}] + \int_0^1 d\lambda{\rm Tr}\left[G_\lambda\frac{d\Sigma_\lambda}{d\lambda}\right]\,,\end{aligned} \tag{6}$$

where $\Sigma_{\lambda=0} = 0$ and $\Phi_{\lambda=0} = 0$ have been used, and $E_{\rm H}[G] = 1/2\int d\mathbf{r}v_{\rm H}(\mathbf{r})n(\mathbf{r})$ is the Hartree energy.

To proceed, the Dyson equation linking G_λ and Σ_λ has to be invoked, which in the current context reads

$$G_\lambda^{-1} = G_s^{-1} - \Sigma_\lambda[G_\lambda] - v_{\rm ext}^\lambda - \lambda v_{\rm H} + v_s \tag{7}$$

where $v_{\rm ext}^\lambda$ is the external potential of the λ-dependent system (with $v_{\rm ext}^{\lambda=1} = v_{\rm ext}$) to keep the density unchanged, and $v_s = v_{\rm ext} + v_{\rm H} + v_{\rm xc}$ is the effective single-particle potential of the KS reference system. From Eq. (7), one gets

$$\begin{aligned}-\frac{d}{d\lambda}\ln G_\lambda^{-1} &= -\frac{d}{d\lambda}\ln\left[G_s^{-1} - \Sigma_\lambda - v_{\rm ext}^\lambda - \lambda v_{\rm H} + v_{\rm s}\right]\\ &= G_\lambda\left[\frac{d}{d\lambda}\Sigma_\lambda + \frac{d}{d\lambda}v_{\rm ext}^\lambda + V_{\rm H}\right]\,.\end{aligned} \tag{8}$$

Using Eq. (8), and denoting $G_{\lambda=1} = G$, $\Sigma_{\lambda=1} = \Sigma$, and $\Phi_{\lambda=1} = \Phi$, one obtains

$$
\begin{aligned}
E =& T_{\mathrm{s}} + \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) + E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\,[\Sigma G] \\
& - \int_0^1 d\lambda \mathrm{Tr}\left[\frac{d}{d\lambda}\ln G_\lambda^{-1} + G_\lambda \frac{d}{d\lambda} v_{\mathrm{ext}}^\lambda + G_\lambda V_{\mathrm{H}}\right] \\
=& T_{\mathrm{s}} + \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) - E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\,[\Sigma G] \\
& - \mathrm{Tr}[\ln G^{-1}] + \mathrm{Tr}[\ln G_s^{-1}] - \int d\mathbf{r} n(\mathbf{r}) \frac{d}{d\lambda} v_{\mathrm{ext}}^\lambda(\mathbf{r}) \\
=& T_{\mathrm{s}} + \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{s}}(\mathbf{r}) - E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\,[\Sigma G] \\
& - \mathrm{Tr}[\ln G^{-1}] + \mathrm{Tr}[\ln G_s^{-1}] \\
=& - E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\,[\Sigma G] - \mathrm{Tr}[\ln G^{-1}], \quad (9)
\end{aligned}
$$

where $G_s = G_{\lambda=0}$ is the reference KS Green function, and

$$
\mathrm{Tr}[\ln G_s^{-1}] = -\sum_i^{\mathrm{occ}} \epsilon_i = -T_s - \int d\mathbf{r} n(\mathbf{r}) v_s(\mathbf{r}), \quad (10)
$$

with ϵ_i being the KS eigenvalues. To derive Eq. (9), we have also used

$$
\begin{aligned}
& \int_0^1 d\lambda \mathrm{Tr}\,[G_\lambda v_{\mathrm{H}}] \\
&= \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int d\mathbf{r} d\mathbf{r}' G_\lambda(\mathbf{r}, \mathbf{r}', i\omega) V_{\mathrm{H}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \\
&= \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{H}}(\mathbf{r}) = 2E_{\mathrm{H}} \quad (11)
\end{aligned}
$$

and similarly

$$
\begin{aligned}
\int_0^1 d\lambda \mathrm{Tr}\left[G_\lambda \frac{dv_{\mathrm{ext}}^\lambda}{d\lambda}\right] &= \int_0^1 d\lambda \int d\mathbf{r} n(\mathbf{r}) \frac{dv_{\mathrm{ext}}^\lambda(\mathbf{r})}{d\lambda} \\
&= \int d\mathbf{r}\,(v_{\mathrm{ext}}(\mathbf{r}) - v_{\mathrm{s}}(\mathbf{r}))\, n(\mathbf{r}) d\mathbf{r}\,, \\
&\qquad\qquad\qquad\qquad\qquad (12)
\end{aligned}
$$

noticing that $v_{\mathrm{ext}}(\mathbf{r}) = v_{\mathrm{ext}}^{\lambda=1}$ and $v_s(\mathbf{r}) = v_{\mathrm{ext}}^{\lambda=0}$.

Eq. (9) clearly indicates the resultant interacting ground-state energy does not depend on the reference state. Making use of the Dyson equation (7) at $\lambda = 1$,

Equivalent expressions to Eq. (9) can be obtained

$$
\begin{aligned}
E =& -E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\,[\Sigma G] - \mathrm{Tr}[\ln\left(G_s^{-1} + v_{\mathrm{xc}} - \Sigma\right)] \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (13) \\
=& -E_{\mathrm{H}}[G] + \Phi[G] - \mathrm{Tr}\left[(G_s^{-1} + v_{\mathrm{xc}})G - 1\right] - \mathrm{Tr}[\ln G^{-1}]. \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (14)
\end{aligned}
$$

Eqs. (9), (13), and (14) are all equivalent when G is a self-consistent solution of the Dyson equation (7). Regarding the energy E as a functional of G, Eq. (13) is known as the Luttinger-Ward functional [1] and Eq. (14) the Klein functional [2]. Eq. (7) in the main paper – the total energy in the form of the Klein functional – is thus derived.

As discussed in the main paper, and in Refs. [3, 4], evaluating the Klein functional under the GW approximation with the noninteracting Green function G_s one obtains the RPA total energy

$$
\begin{aligned}
E^{\mathrm{RPA}} =& -E_{\mathrm{H}}[G_s] + \Phi^{GW}[G_s] - \mathrm{Tr}\,[v_{\mathrm{xc}} G_s] - \mathrm{Tr}[\ln G_s^{-1}] \\
=& T_s + \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) + E_{\mathrm{H}}[G_s] + E_{\mathrm{x}}[G_s] + E_{\mathrm{c}}^{\mathrm{RPA}}[G_s], \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (15)
\end{aligned}
$$

where we have been used

$$
-\mathrm{Tr}\,[v_{\mathrm{xc}} G_s] - \mathrm{Tr}[\ln G_s^{-1}] = T_s + \int d\mathbf{r} n(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) + 2E_{\mathrm{H}} \quad (16)
$$

and

$$
\begin{aligned}
\Phi^{GW}[G_s] &= \sum_{n=1}^{\infty} \frac{1}{2n} \mathrm{Tr}\left[\Sigma^{(n)}[G_s] G_s\right] \\
&= \frac{1}{2}\mathrm{Tr}\,[\Sigma_{\mathrm{x}} G_s] - \sum_{n=2}^{\infty} \frac{1}{2n} \mathrm{Tr}\,[(v\chi_s)^n] \\
&= E_{\mathrm{x}} + E_{\mathrm{c}}^{\mathrm{RPA}} \quad (17)
\end{aligned}
$$

with the Σ_{x} being the exact-exchange self-energy.

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