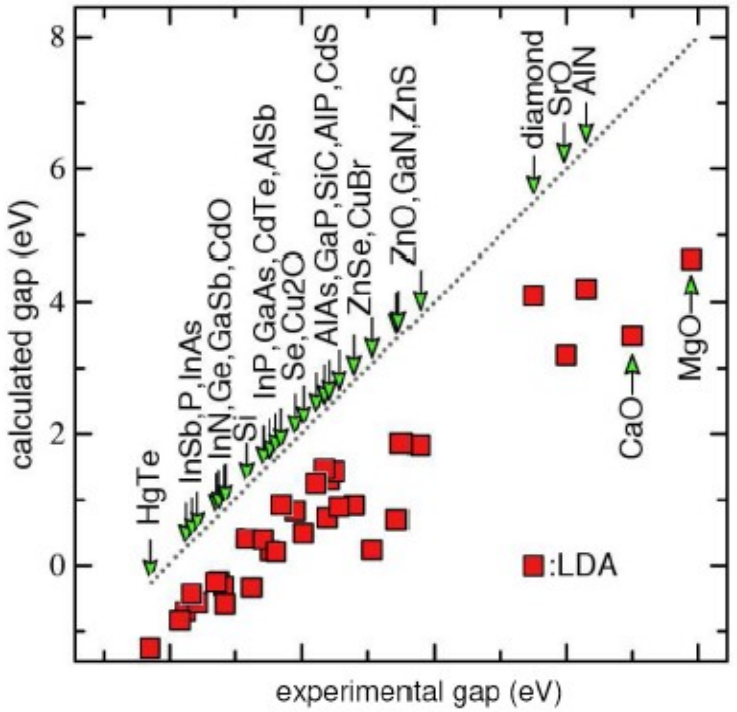
Introduçao ao Método GW.

Ana M. Valencia.

IF-USP.

Gap de Energia



adapted from M. van Schilfgaarde *et al.*, PRL **96** (2006).

$$E_{gap} = I - A$$

Indo além da teoria do gás de elétrons livres...

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†
Argonne National Laboratory, Argonne, Illinois
(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

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Indo além da teoria do gás de elétrons livres...

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The results of this paper also provide *a new approach to, and qualitative conclusions regarding, the general type of excitation spectra, which correspond to a single excited electron outside or a hole in a closed-shell structure.*

Indo além da teoria do gás de elétrons livres...

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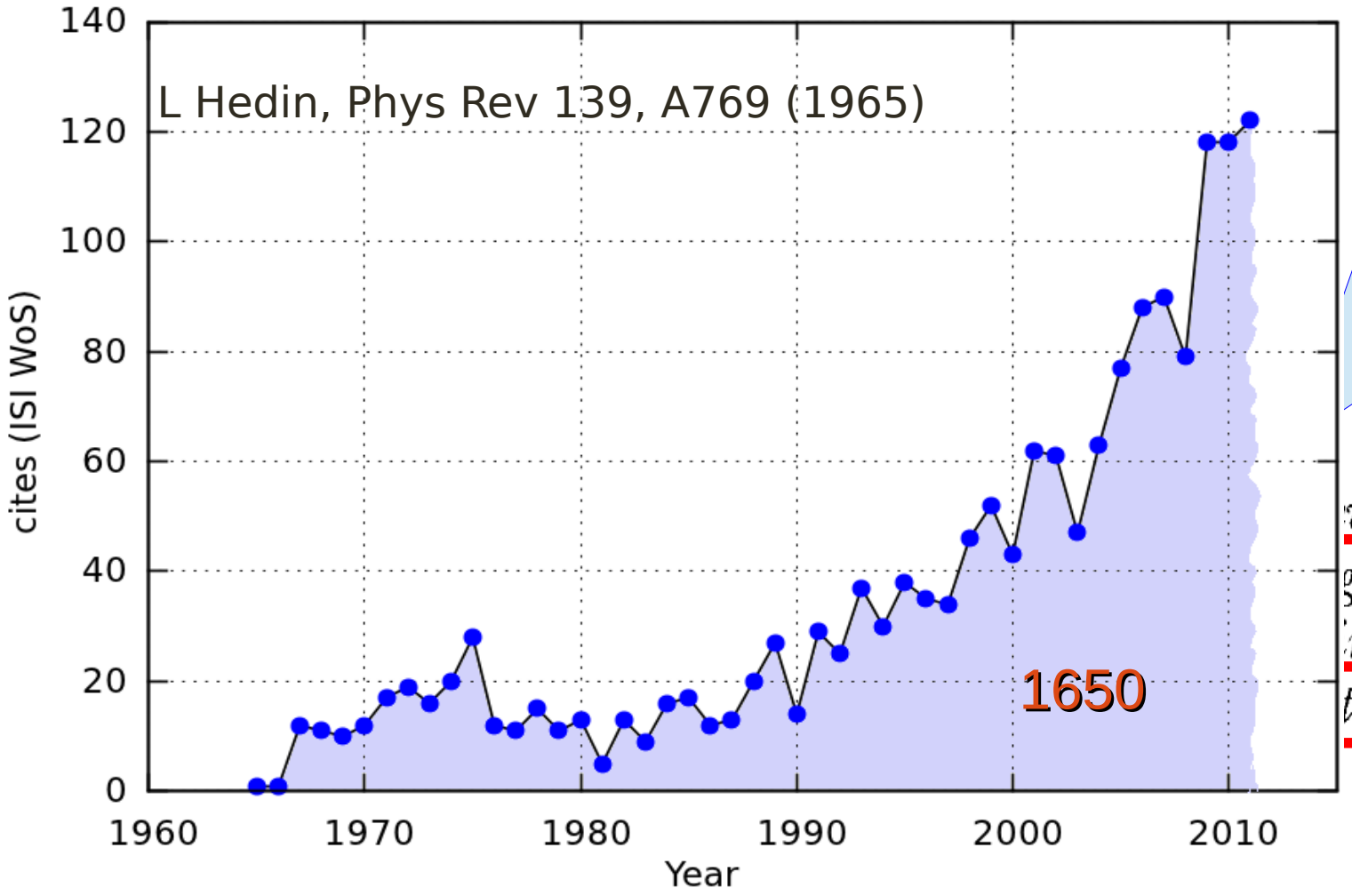

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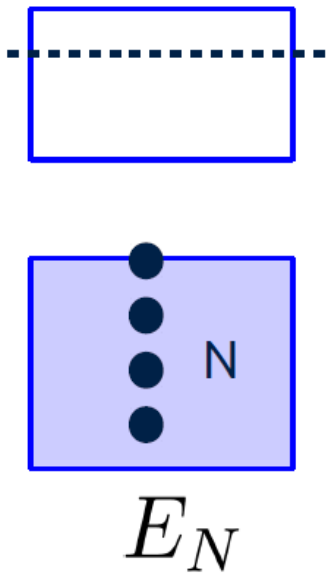
Fotoemissão, energias de excitação

INÍCIO



Fotoemissão, energias de excitação

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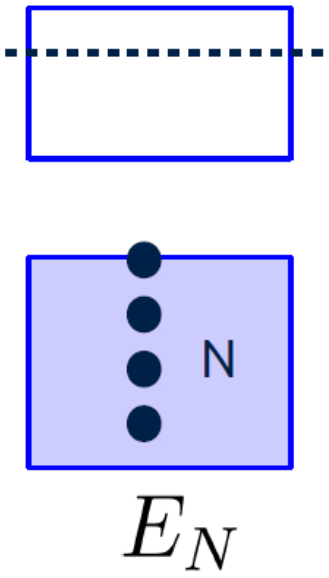
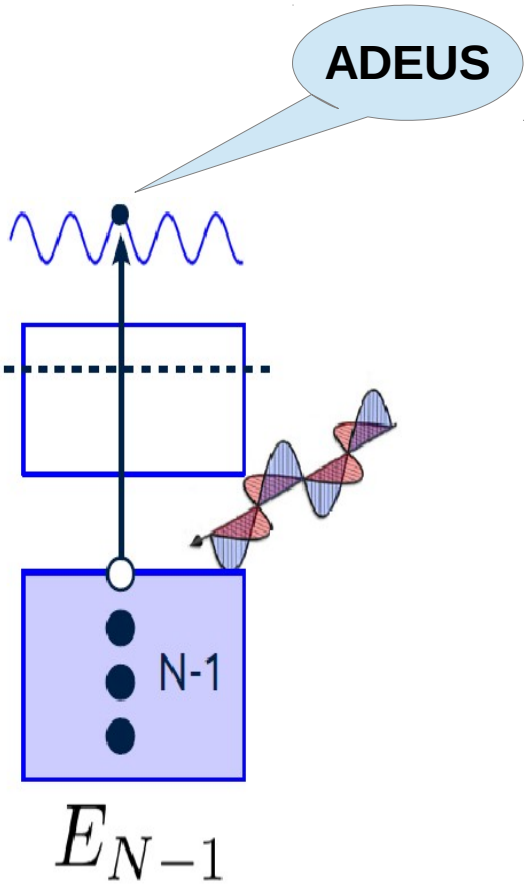
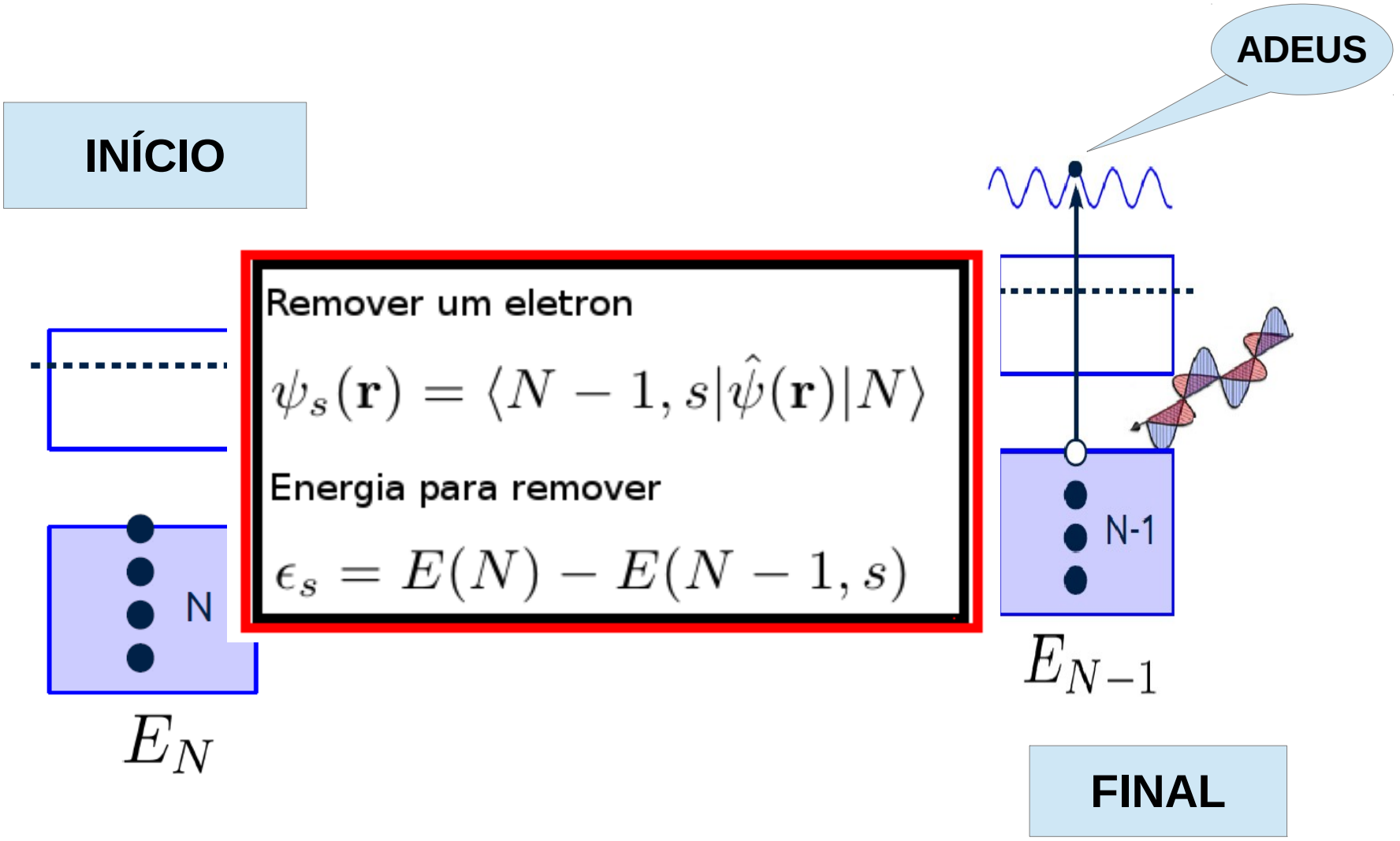




FINAL

Fotoemissão, energias de excitação



Fotoemissao inverso, energias de excitaçao

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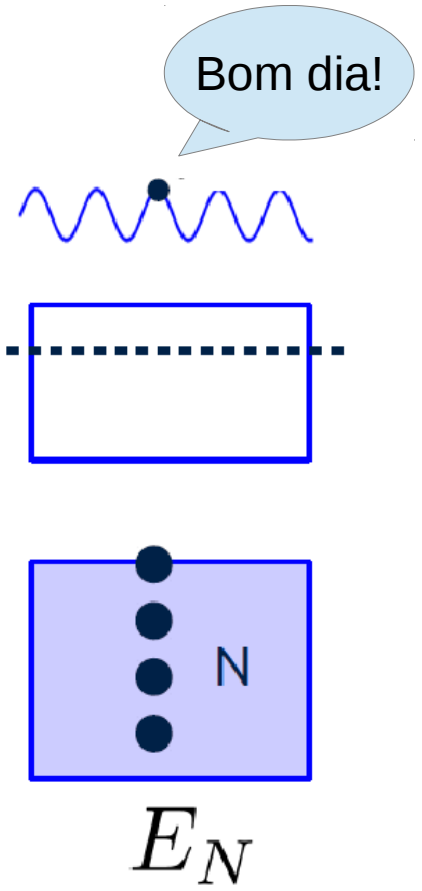

Fotoemissão inverso, energias de excitação

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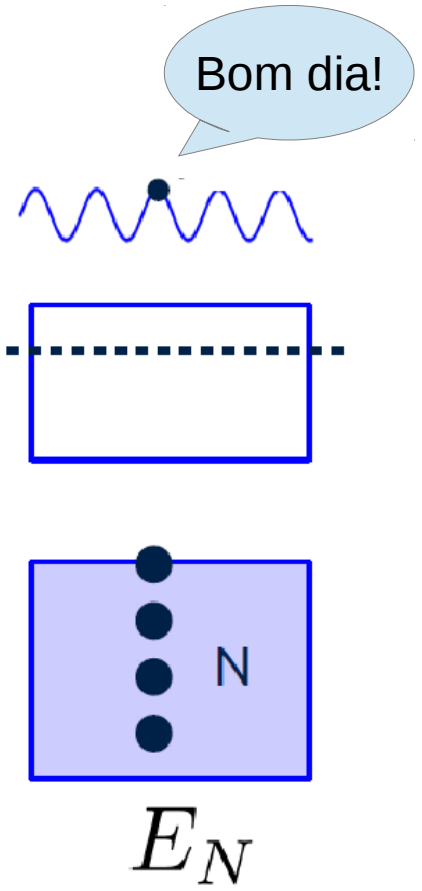

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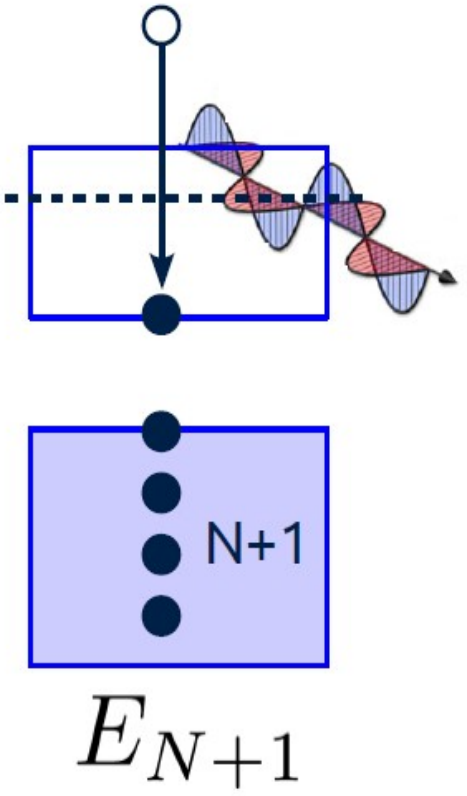

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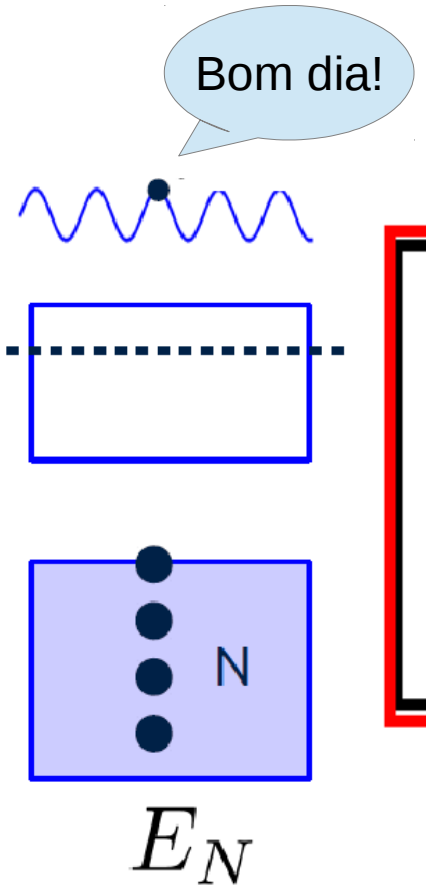
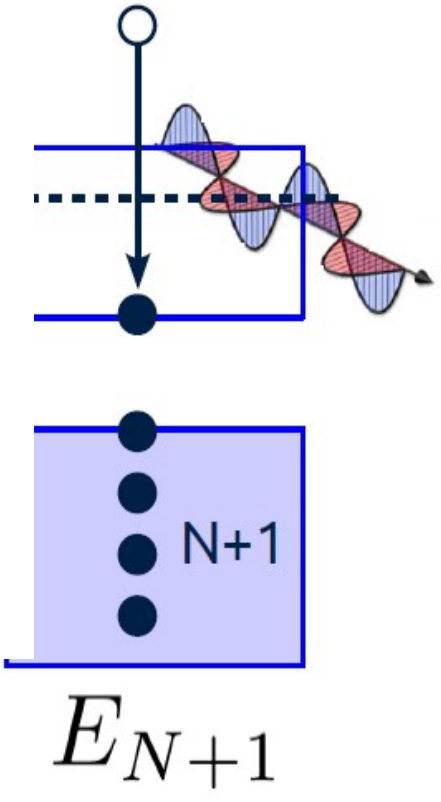


Adição de elétron.

$$\psi_s(\mathbf{r}) = \langle N|\hat{\psi}(\mathbf{r})|N+1,s\rangle$$

Energia de adição

$$\epsilon_s = E(N+1,s) - E(N)$$



Função de Green para uma partícula.

A função contém o espectro de exitação total.

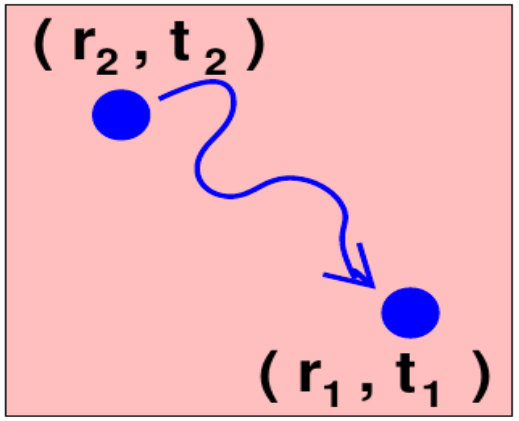
$$iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = \langle N| T\left[\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)\right] |N\rangle$$

$$t_1 > t_2 \Rightarrow iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = \langle N|\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)|N\rangle$$

$$t_1 < t_2 \Rightarrow iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = -\langle N|\psi^\dagger(\mathbf{x_2}, t_2)\psi(\mathbf{x_1}, t_1)|N\rangle$$

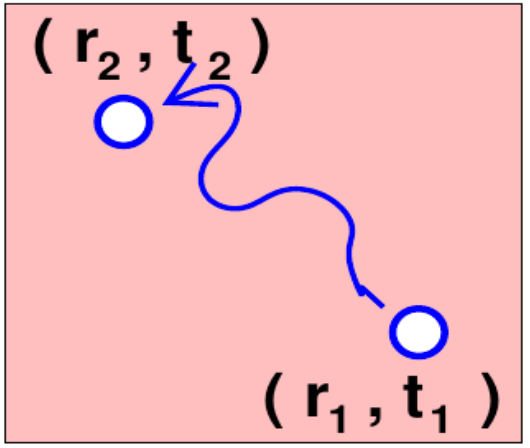
Função de Green para uma partícula.

$$t_1 > t_2$$
$$\langle N|\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)|N\rangle$$



Amplitude de probabilidade de que um eletrón criado en 2 se propage até 1.

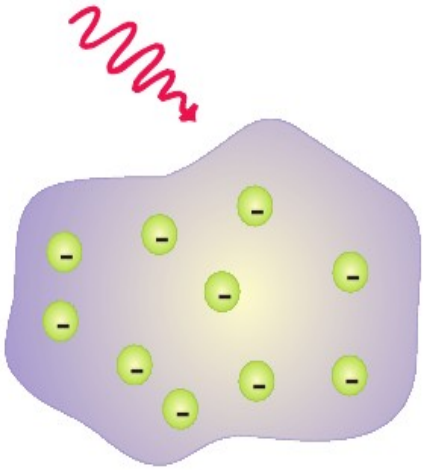
$$t_1 < t_2$$
$$-\langle N|\psi^\dagger(\mathbf{x_2}, t_2)\psi(\mathbf{x_1}, t_1)|N\rangle$$



Amplitude de probabilidade de encontrar un bucaco en 2 se retiramos um elétron en 1

Quasipartícula

...



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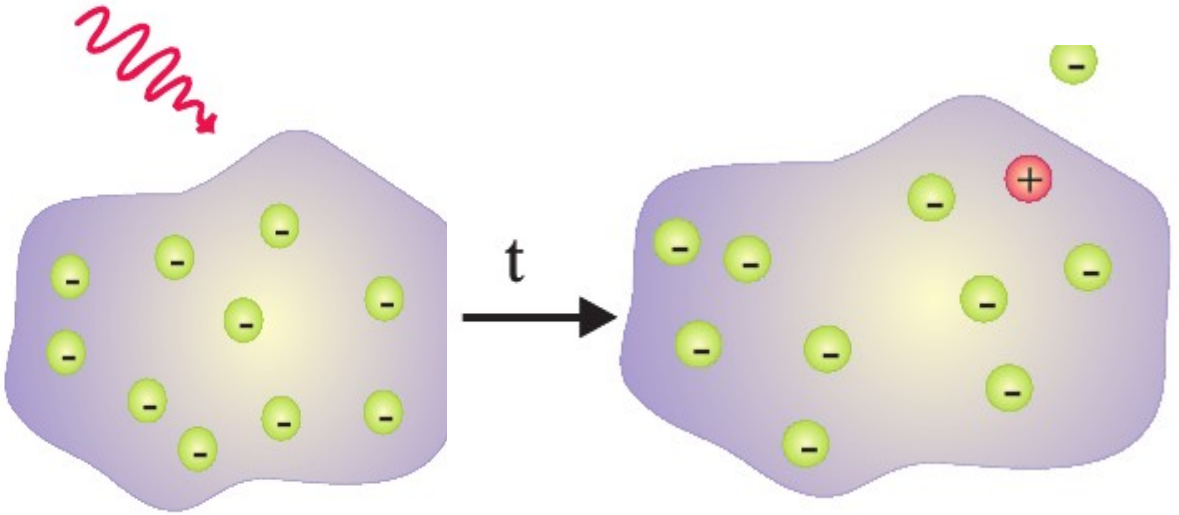

Sistema polarizado

Quasipartícula

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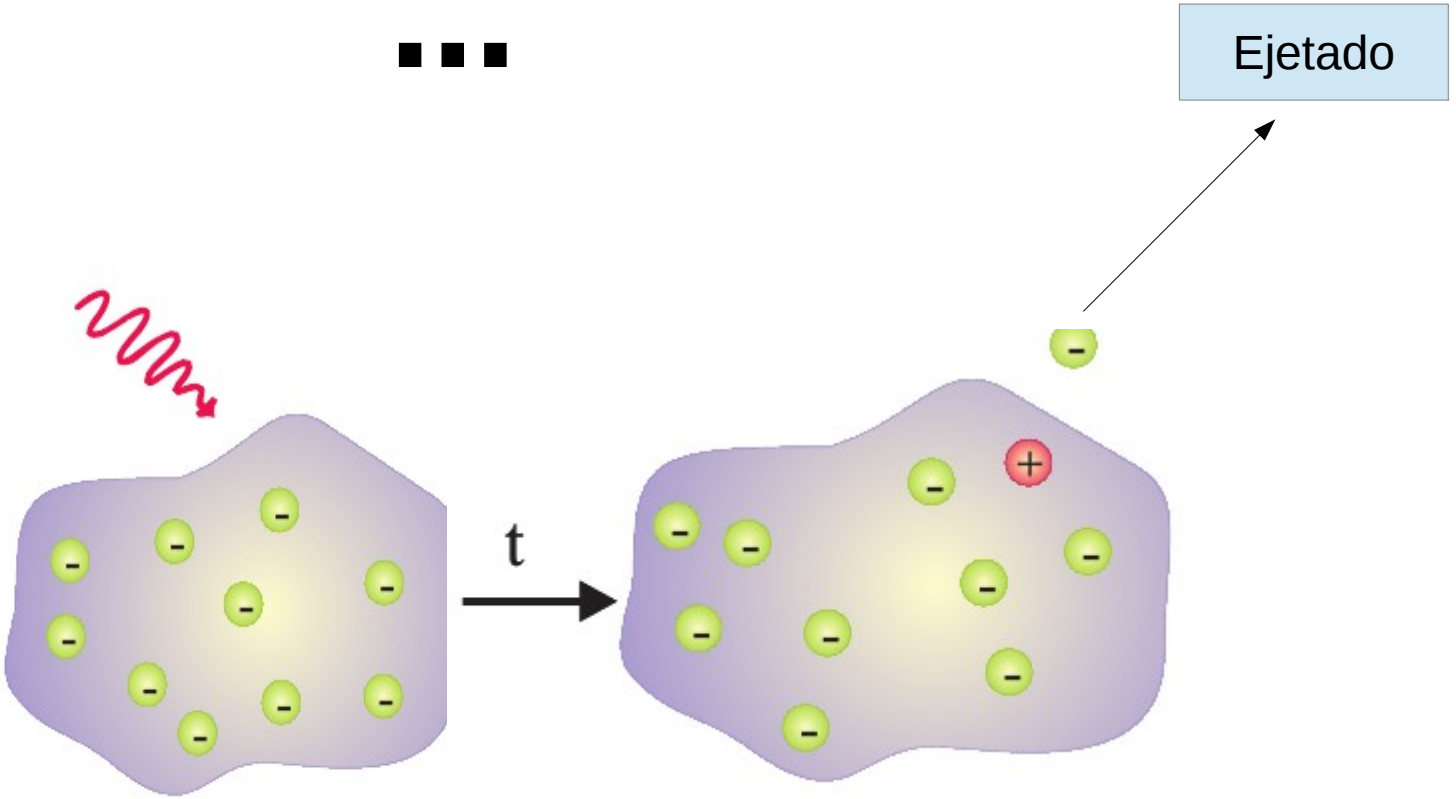

Sistema polarizado

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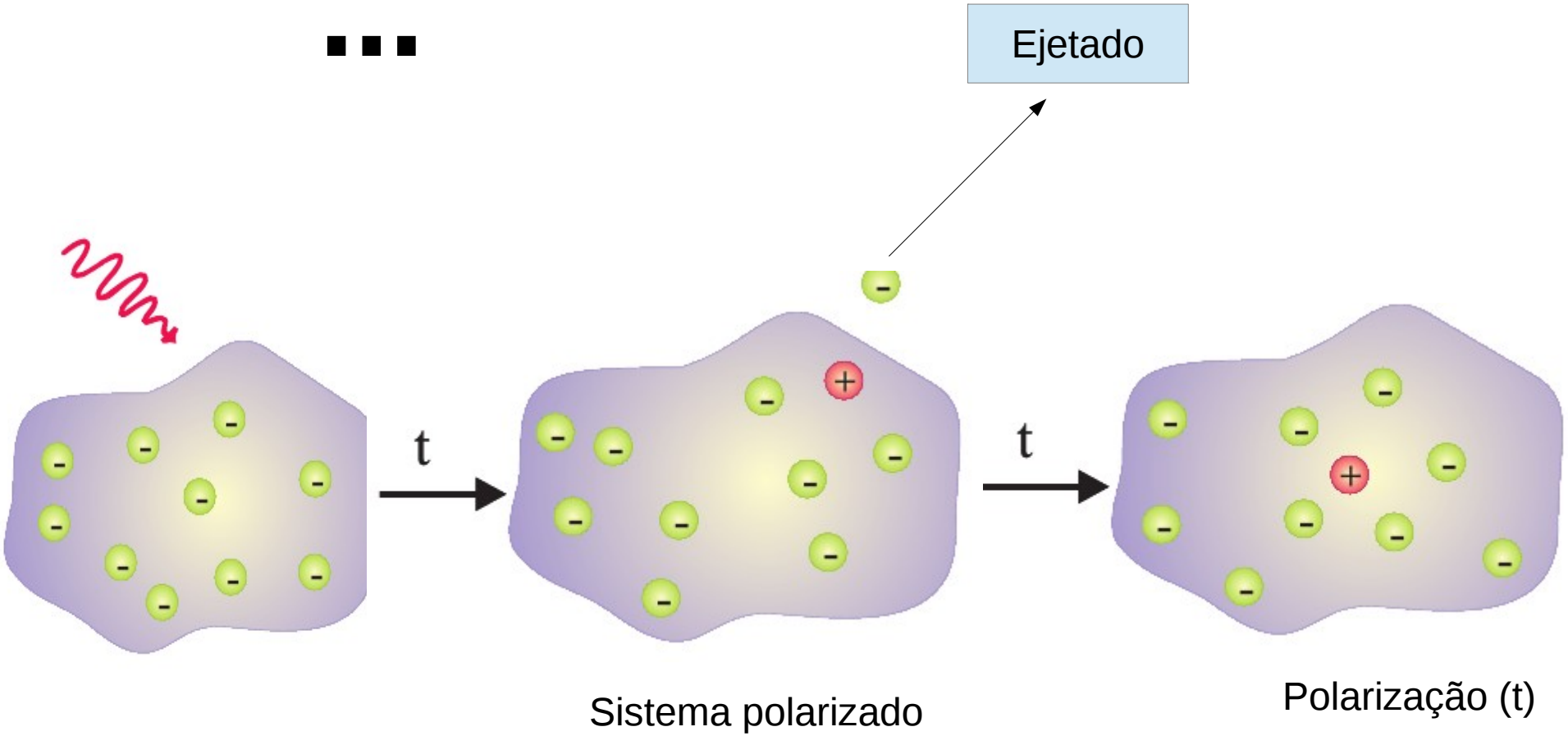

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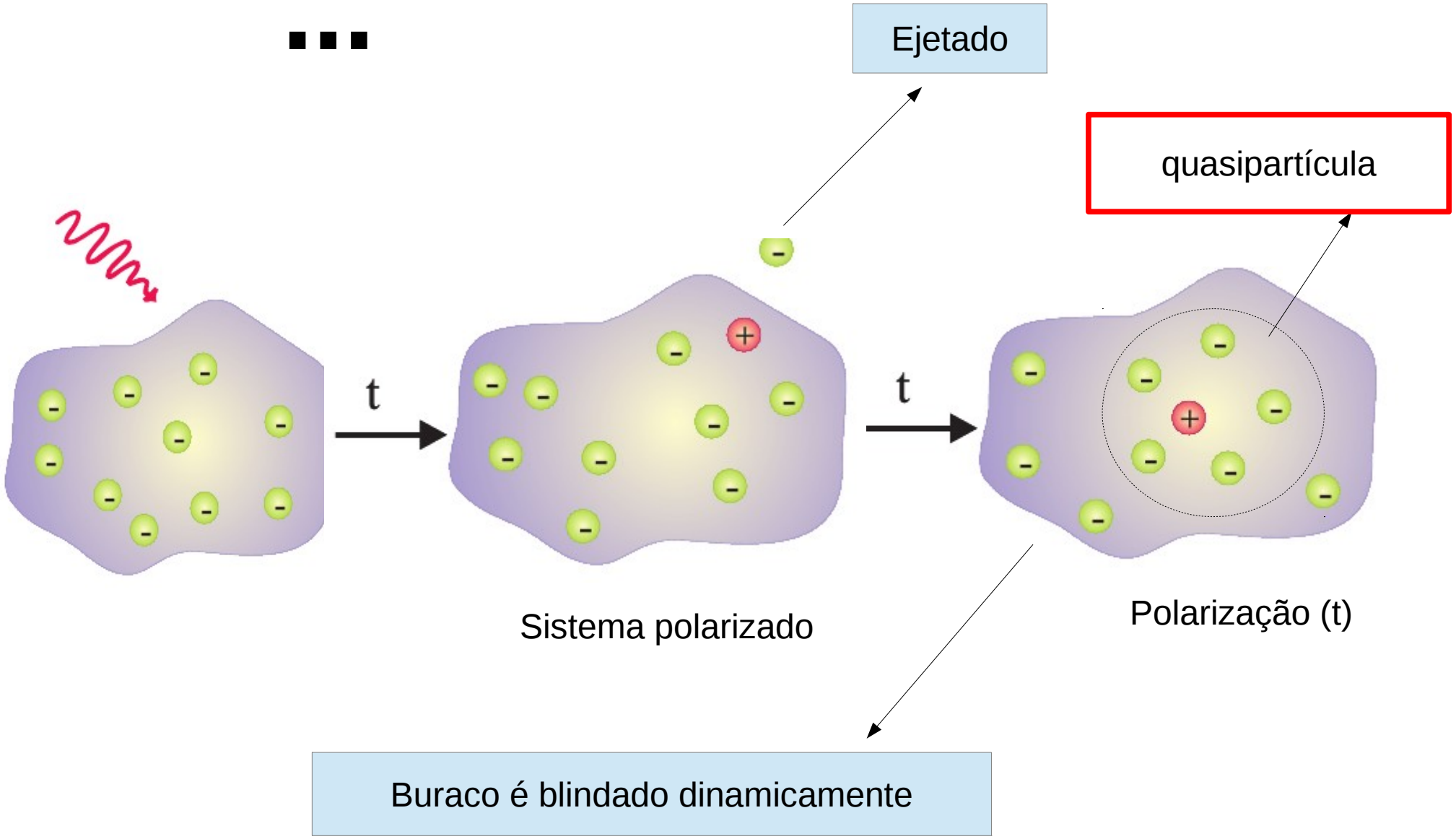


Equações de Hendin.

$$\hat{H} = \sum_i \left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2}\sum_{ij} v(\mathbf{r}_i, \mathbf{r}_j)$$

Hamiltoniano de muito corpos

$$\hat{H} = \int \hat{\psi}^\dagger(\mathbf{r})\hat{h}(\mathbf{r})\hat{\psi}(\mathbf{r})d^3r + \frac{1}{2}\iint \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')v(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})d^3r\, d^3r'$$

Onde, operador de uma particula,

$$\hat{h}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r})\,.$$

Eq. de movimento da função de Green

$$i\hbar\frac{\partial}{\partial t}G(\mathbf{r}t,\mathbf{r}'t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') + \hat{h}(\mathbf{r})G(\mathbf{r}t,\mathbf{r}'t')$$
$$-\frac{i}{\hbar}\int v(\mathbf{r},\mathbf{r}'')\left\langle \Psi_0^N \left| \hat{T}\left[\hat{\psi}^\dagger(\mathbf{r}'',t)\hat{\psi}(\mathbf{r}'',t)\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')\right] \right| \Psi_0^N \right\rangle d^3r''$$

$$i\hbar\frac{\partial}{\partial t_1}G(12) = \delta(12) + \hat{h}(1)G(12) - i\hbar\int v(1^+3)G(1323^+)d3\,.$$

sendo $3^+ = (r_3, t_3^+)$, e é trazida já a função de Green de duas partículas

$$G_2(1,2,3,4) = (-i)^2\langle N|\mathcal{T}[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(3)\hat{\psi}^\dagger(4)]|N\rangle$$

Escrevemos a função de Green de duas partículas como o producto de funções de Green de uma partícula.

$$G_2(1,3,3^+,2) = G(1,2)G(3,3^+) + \Lambda$$

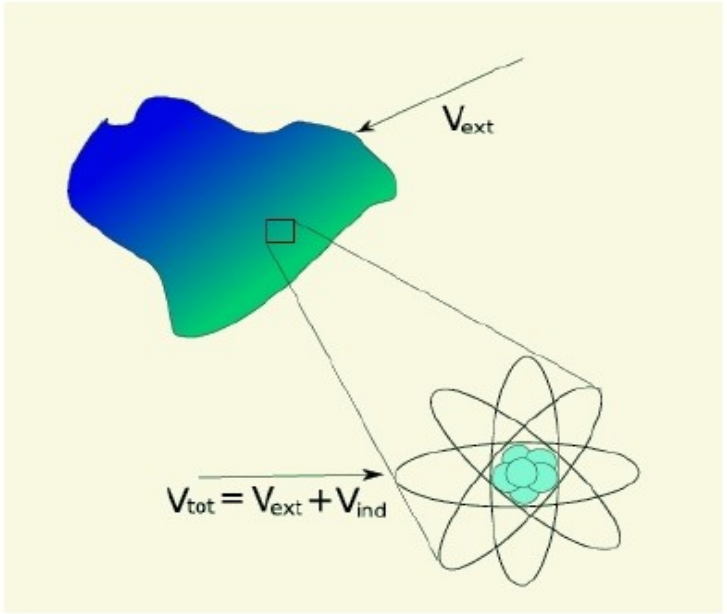
Voltando à equação de movimento da função de Green,

$$\left[i\hbar\frac{\partial}{\partial t_1} - \hat{h}_0(1)\right] G(12) - \int \Sigma(13)G(32)d3 = \delta(12) ;$$

Para o caso do um sistema não interagente temos:

$$\left[i\hbar\frac{\partial}{\partial t_1} - \hat{h}_0(1)\right] G_0(12) = \delta(12)$$

Equação de Dyson $G(12) = G_0(12) + \iint G_0(13)\Sigma(34)G(42)d3\,d4\,.$



A relação da densidade a alterações no potential externo é governada pela função resposta.

$$R(12) = \left.\frac{\delta n(1)}{\delta U(2)}\right|_{U=0}$$

O potencial externo e o potencial de Coulomb criado pela carga induzida, pode ser escrito como um potencial efetivo.

$$U_{\text{eff}}(1) = U(1) + \iint v(13)\, R(32)\, U(2) d2\, d3\,,$$

$$\varepsilon^{-1}(12) = \left.\frac{\delta U_{\text{eff}}(1)}{\delta U(2)}\right|_{U=0} = \delta(12) + \int v(13) R(32) d3\,.$$

Potencial externo → Função dielétrica → polarização

$$W(12) = \int \varepsilon^{-1}(13) v(32) d3 = v(12) + \iint v(13) P(34) W(42) d3\, d4$$

Resumindo, as equações de Hendin são:

$$\Sigma(12) = i \int d(34) G(14) W(1^{+}3) \Gamma(423)$$

$$W(12) = v(12) + \int d(34) v(42) P(34) W(13)$$

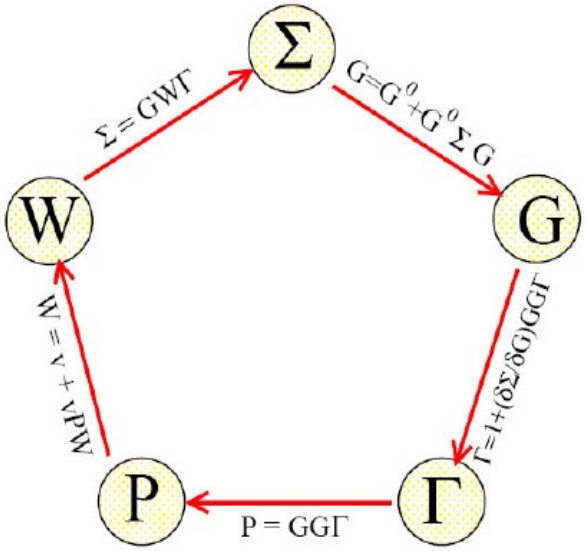
Screened Coulomb

$$P(12) = -i \int d(34) G(23) G(42) \Gamma(341)$$

polarização

$$\Gamma(123) = \delta(12)\delta(13) + \int d(4567) \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(673)$$

→ **Tudo em termo do G!!**



L Hedin, Phys Rev 139, A769 (1965)

GW

L Hedin, Phys Rev 139, A769 (1965)

$$\Sigma(12) = i \int d(34) G(14) W(1^+3) \Gamma(423)$$

$$W(12) = v(12) + \int d(34) v(42) P(34) W(13)$$

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$$\Gamma(123) = \delta(12)\delta(13) + \int d(4567) \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(673)$$

Aproximação G0W0

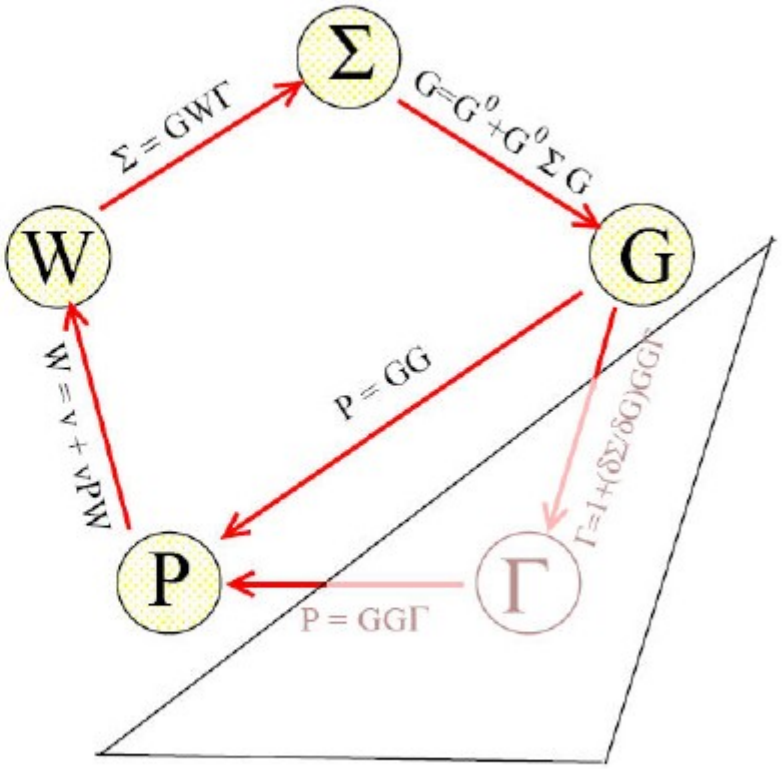
Por exemplo, iniciando com a aproximação $\Sigma = 0$,

$$
\begin{aligned}
G(1,2) &= G_0(1,2) \\
\Gamma(1,2;3) &= \delta(1,2)\delta(1,3) \\
P(1,2) &= -i\hbar G_0(1,2)G_0(2,1) \\
W(1,2) &= v(1,2) + v(1,4)P(4,5)W(5,2) \\
\Sigma(1,2) &= i\hbar G_0(1,2)W(1,2)
\end{aligned}
$$

Em virtude da forma de Σ na última equação do ciclo, surgiu o nome da aproximação como "one-shot GW" e ultimamente chamada explicitamente G_0W_0. Utilizando este novo Σ poderíamos reiniciar o ciclo, obtendo novos valores para G, Γ, P, W e finalmente outro Σ; entretanto o que se verifica é que um ciclo já apresenta ótimas correções, e é o que se faz na prática.

Aproximação G0W0

$$\Sigma = iGW$$
$$G = G_0 + G_0 \Sigma G$$
$$\Gamma = 1$$
$$P = -iGG$$
$$W = v + vPW$$



L. Hedin, Phys. Rev. **139** (1965)

Hartree-Fock

$$\Sigma(12) = iG(12)v(12)$$

$$\Sigma(12) = i\int d(34)G(14)W(1^+3)\Gamma(423)$$

$$W(12) = v(12) + \int d(34)v(42)P(34)W(13)$$

$$P(12) = -i\int d(34)G(23)G(42)\Gamma(341)$$

$$\Gamma(123) = \delta(12)\delta(13) + \int d(4567)\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)$$

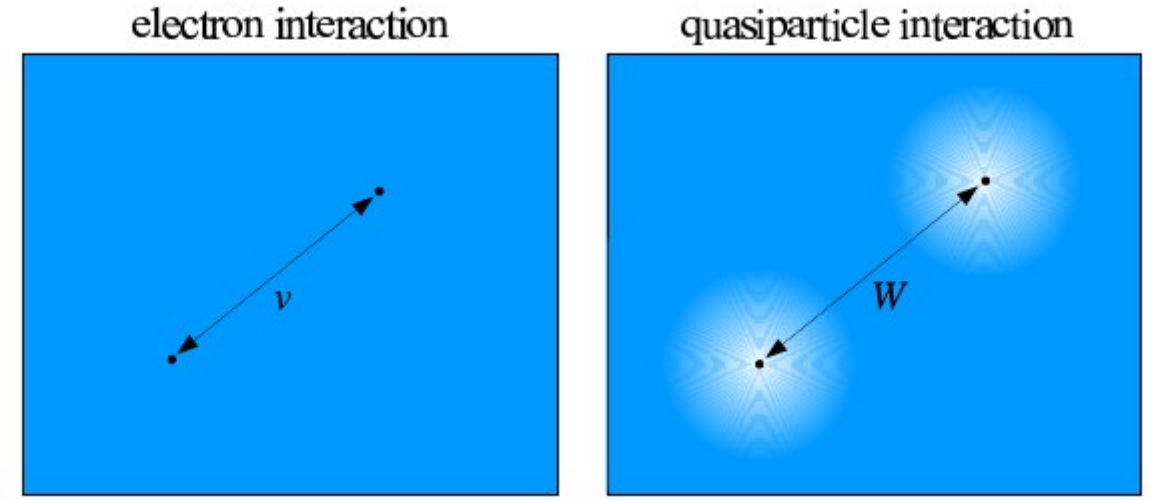
Significado Físico

Autoconsistente energia Hartree-Fock.

$$\Sigma(1,2) = iG(1,2)v(1^+,2)$$

Autoconsistente energia GW.

$$\Sigma(1,2) = iG(1,2)W(1^+,2)$$



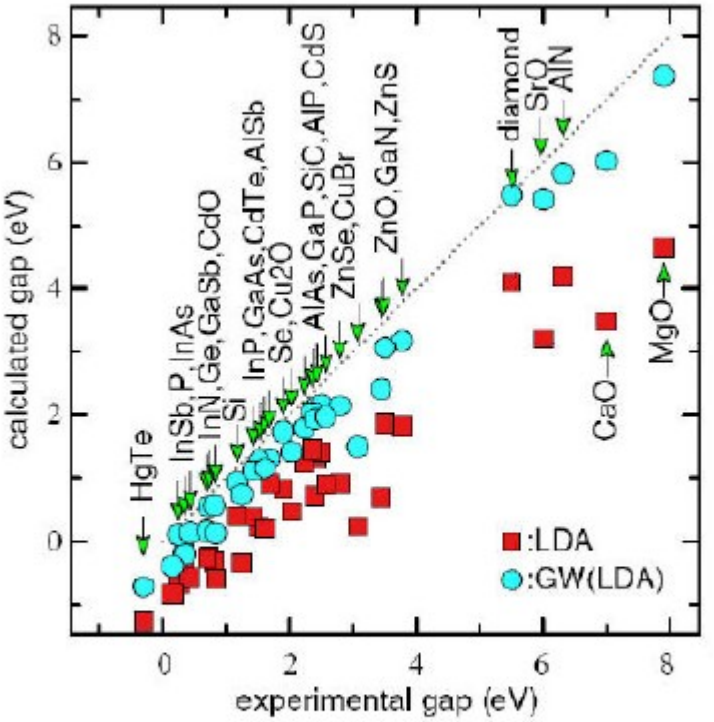
http://www.fz-juelich.de/nic-series/volume31

O sistema original fortemente interagente é representado por quasipartícula, fracamente interagente.

W é um potencial de curto alcance, interação fraca.

V é um potencial de largo alcance, interação forte.

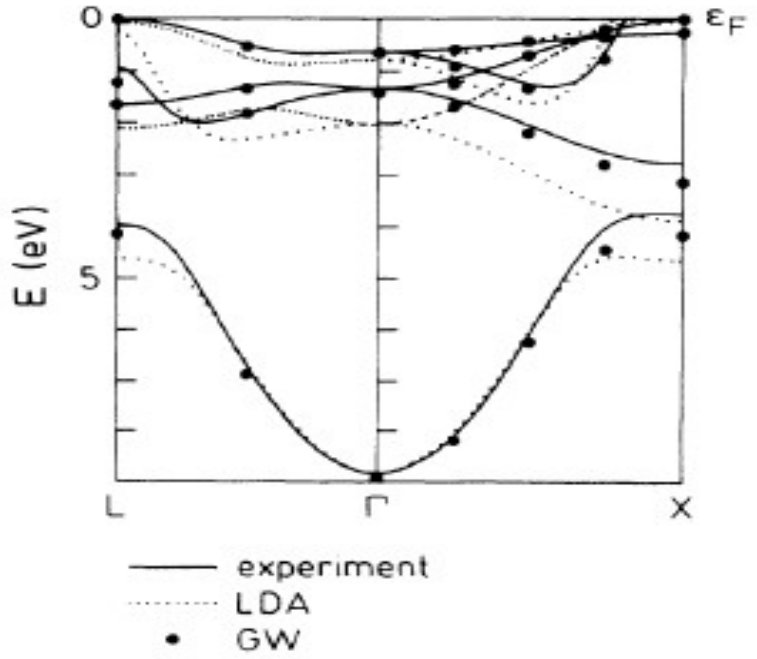
Depois de uma correção de primeira ordem G0W0



M. van Schilfgaarde *et al.*, PRL **96** (2006).

Depois de uma correção de primeira ordem G0W0

Nickel



from F. Aryasetiawan, PRB **46** 13051 (1992).