

# Brueckner Orbitals and Density-Functional Theory

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## Abstract

By means of Many-Body Perturbation Theory (MBPT) it is shown that minimizing the energy expectation value of a closed-shell system in a certain order of the perturbation expansion by varying the partitioning of the Hamiltonian, leads to a zeroth-order function, which – as the order of perturbation increases and provided the expansion converges properly – approaches a determinant of Brueckner orbitals. It is also shown that the energy eigenvalues of the Brueckner orbitals represent the corresponding ionization energies of the system, including orbital-relaxation and correlation effects to all orders of perturbation theory. This is a *generalization of the Koopmans theorem* in Hartree-Fock theory. The MBPT treatment is used for a discussion of the Density-Functional Theory (DFT), and a new model is proposed – referred to as the *Brueckner-Kohn-Sham* (BKS) scheme – where also the electron correlation is included in the functional. This leads to a non-local exchange-correlation potential, quite similar to that of Brueckner orbitals (BO), implying that the orbitals of the new scheme are essentially BO. Arguments are given that also the orbitals of other schemes with a purely local potential, such as the standard Kohn Sham (KS) scheme, would be close to BO. This has been conjectured by Heßelmann and Jansen (J. Chem. Phys. **112**, 6949 (2000)), and the present work gives more direct evidence of that. This might explain the recent observations that the KS orbitals and energy eigenvalues do have more physical significance than was originally anticipated.

## 1 Introduction

Per-Olov Löwdin has in a series of seminal papers laid down the foundation of modern theory of *Self-Consistent-Fields* (SCF) and of *Many-Body Perturbation Theory* (MBPT) [1, 2, 3, 4, 5, 6, 7]. In the paper [6], entitled '*Studies in Perturbation Theory. V. Some Aspects of Exact Self-Consistent Field Theory*', he introduced into quantum chemistry the important concept of *Brueckner orbitals* and formulated the *Brillouin-Brueckner condition*. In the present paper we shall be particularly concerned with MBPT and the Brueckner orbitals and their relation to the *Density-Functional Theory* (DFT).

The MBPT was in the 1950's and 1960's developed in the form of the *linked-cluster* or *linked diagram expansion*, initially formulated for closed-shell systems by Brueckner [8] and Goldstone [9] and later extended, particularly in nuclear physics, to degenerate open-shell systems by Brandow [10], Brown, Kuo and others [11, 12, 13, 14] and also to general quasi-degenerate systems [15, 16]. The *Coupled-Cluster Approach* (CCA) of MBPT or *Exponential Ansatz* was developed during the same period, first in nuclear theory by Hubbard, Coster and Kümmel [17, 18, 19, 20, 21] and later in quantum chemistry by Čížek, Paldus and others [22, 23, 24, 16, 25].

As an alternative to MBPT and CCA, the DFT has in the last 10-15 years developed into an extremely popular and useful tool for computational quantum chemistry. DFT started actually already in the 1920's by the development of the statistical atomic model by Thomas and Fermi [26,

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27]. In 1951 Slater [28, 29] introduced the local statistical exchange approximation, which formed the beginning of the *Local Density Approximations* (LDA). The modern form of DFT started by the fundamental papers by Hohenberg and Kohn [30] and by Kohn and Sham [31]. Later the formalism has been extended and improved by many groups. The major formal improvement was the introduction of the *constrained search* by Levy in 1979 [32].

In the original Kohn Sham (KS) scheme, the electrons move independently in a *local* potential, which represents – apart from the Coulomb and external fields – also the electron exchange and correlation effects [33]. Although the KS potential can in principle represent the exchange-correlation in an exact way, no schemes have been devised for its evaluation apart from the crude local-density approximation (LDA) and the gradients variants (Generalized Gradient Approximations, GGA) [34, 35, 36, 37, 38]. A scheme which treats the *electron exchange* part exactly within the Kohn-Sham picture has recently been developed and is referred to as the EXX scheme. It has first been suggested as an approximation to the Hartree-Fock method under the name *Optimized Exchange Potential* (OEP) [39]. Later it was derived within a Kohn-Sham framework [40, 41], and it was shown to yield the exact local KS exchange.

It was found a number of years ago that the LDA and GGA results can be considerably improved by including into the potential a fraction of a *non-local exchange potential*, yielding schemes referred to as *hybrid* schemes [42, 43, 44, 45, 46, 47, 48]. In recent years a number of formal schemes have been developed by Levy, Görling and others [49, 50], which can be regarded as *Generalized Kohn-Sham* (GKS) schemes and which will form the starting point of the present work. In a scheme known as the *Hartree-Fock-Kohn-Sham* (HF-KS) scheme [49] the electron exchange is treated exactly by means of a *non-local* potential. The electron correlation effect is as in the original KS scheme treated by means of a local potential. In the present paper we will extend the arguments in order to include also most of the *electron correlation* into the model. This leads to a scheme, which we will refer to as the *Brueckner-Kohn-Sham* (BKS) scheme, with a *non-local exchange-correlation potential*, which we show is quite similar to that of Brueckner orbitals (BO). This implies that the orbitals of this scheme are essentially Brueckner orbitals. It is well-known that BO are more *'physical'* than HF orbitals, in the sense that experimental single-electron properties are much better represented by such orbitals [51, 52, 53, 54]. As a consequence, the orbitals and eigenvalues of the BKS scheme would have definite physical significance. Arguments will be given that the orbitals of other schemes, such as the standard Kohn-Sham procedure, also are similar to Brueckner orbitals – as has recently been conjectured by Heßelmann and Jansen [54]. This may be the case also for orbitals generated by means of a local exchange potential of Slater type, where it has been found that single-particle properties, like the hyperfine structure, often agree better with experiments than do the HF results [51].

The present paper will be organized as follows. In the first MBPT part we shall study the minimization of the energy expectation value of a closed-shell system in a certain order of perturbation theory, and it will be shown that this leads at increasing order to a zeroth-order determinant of Brueckner orbitals. In the second part we shall compare the minimization of the energy expectation value in the MBPT treatment with the energy minimization performed in the Density-Functional Theory (DFT). Minimizing the energy functional of such models have great similarities with minimizing the energy expectation value in MPBT, and this will be our starting point for comparing the two many-body procedures.

## 2 Basic Many-Body Theory

### 2.1 General

We consider an  $N$ -electron system with the Hamiltonian (using Hartree atomic units,  $m = e = \hbar = 4\pi\epsilon_0 = 1$ )

$$H = \hat{T} + \hat{W} + \hat{V}_{\text{ext}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i), \quad (1)$$

where  $\hat{T}$  is the kinetic-energy operator,  $\hat{W}$  the electron-electron interaction and  $\hat{V}_{\text{ext}}$  the interaction with the external (normally the nuclear) field. In treating such a system by means of perturbation theory, the Hamiltonian is partitioned into a *zeroth-order Hamiltonian*,  $H_0$ , and a *perturbation*  $H'$  [16],

$$H = H_0 + H', \quad (2)$$

where

$$\begin{aligned} H_0 &= \hat{T} + \hat{V}_{\text{ext}} + \hat{U} = \sum_{i=1}^N \left\{ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + u \right\}_i = \sum_{i=1}^N h_0(i) \\ H' &= -\hat{U} + \hat{W} = \sum_{i=1}^N -u_i + \sum_{i<j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \end{aligned} \quad (3)$$

The potential  $\hat{U} = \sum_{i=1}^N u_i$  – which can be local or non-local – is hermitean but otherwise optional. The eigenfunctions of the zeroth-order Hamiltonian

$$H_0 \Phi^A = E_0^A \Phi^A \quad (4)$$

can be expressed in the form of *Slater determinants*,

$$\Phi^A = \frac{1}{\sqrt{N!}} \det \{ \phi_a(\mathbf{r}_1) \cdots \phi_n(\mathbf{r}_N) \}, \quad (5)$$

formed of spin-orbitals, which are eigenfunctions of  $h_0$ ,

$$h_0 \phi_i = \varepsilon_i \phi_i. \quad (6)$$

It should be noted that the partitioning above is not unique, since the choice of the potential  $u$  is essentially free. We shall utilize this freedom in the following.

In general MBPT we consider a number ( $d$ ) of eigenstates of the system [16]

$$H \Psi^a = E^a \Psi^a \quad (a = 1, 2, \dots, d), \quad (7)$$

which form the *target space* (T). The corresponding zeroth-order or model functions,  $\Psi_0^a$ , form a *model space* (D), and a *wave operator* transforms the model functions into the corresponding target functions,

$$\Psi^a = \Omega \Psi_0^a \quad (a = 1, 2, \dots, d). \quad (8)$$

The Schrödinger equation of the target states can then be written

$$H \Omega \Psi_0^a = E^a \Omega \Psi_0^a \quad (a = 1, 2, \dots, d). \quad (9)$$

We define an *effective Hamiltonian*,  $H_{\text{eff}}$ , by means of the relation

$$H_{\text{eff}} \Psi_0^a = E^a \Psi_0^a \quad (a = 1, 2, \dots, d). \quad (10)$$

It follows from the definition that this operator has the properties

$$P H_{\text{eff}} P = H_{\text{eff}} P \quad \text{and} \quad Q H_{\text{eff}} P = 0, \quad (11)$$

where  $P$  is the projection operator for the model space and  $Q$  for the complementary space,

$$Q = 1 - P. \quad (12)$$

The exact energy of the target states is given by

$$E^a = \langle \Psi_0^a | H_{\text{eff}} | \Psi_0^a \rangle, \quad (13)$$

assuming the model states to be normalized to unity. The form of the effective Hamiltonian depends on the scheme of normalization, as will be discussed further below.

Using the effective Hamiltonian, the Schrödinger equation (9) can be expressed

$$H\Omega\Psi_0^a = \Omega H_{\text{eff}}\Psi_0^a \quad (a = 1, 2, \dots, d). \quad (14)$$

Since this relation is valid for all model states (which are assumed to span the entire model space), we can write it in the form of an *operator equation*,

$$\boxed{H\Omega P = \Omega H_{\text{eff}} P = \Omega P H_{\text{eff}} P.} \quad (15)$$

We shall refer to this equation as the *Bloch equation* [55, 56, 16, 25]. With the partitioning (2), the Bloch equation (15) becomes

$$[\Omega, H_0]P = (H'\Omega - \Omega P H'_{\text{eff}})P, \quad (16)$$

where  $H'_{\text{eff}}$  is the *effective interaction*, defined by

$$H_{\text{eff}}P = PH_0P + H'_{\text{eff}}P. \quad (17)$$

We shall work here in *intermediate normalization* (IN), where  $P\Omega P = P$  and

$$H_{\text{eff}} = PH\Omega P = PH_0P + PH'\Omega P \quad \text{and} \quad H'_{\text{eff}} = PH'\Omega P. \quad (18)$$

The Bloch equation then becomes

$$[\Omega, H_0]P = (H'\Omega - \Omega P H'\Omega)P. \quad (19)$$

This form can be used to generate an order-by-order expansion, such as the generalized Rayleigh-Schrödinger expansion [15, 16],

$$\begin{aligned} \Omega &= \Omega_0 + \Omega^{(1)} + \Omega^{(2)} + \dots \\ [\Omega^{(n)}, H_0]P &= (H'\Omega - \Omega P H'\Omega)^{(n)}P. \end{aligned} \quad (20)$$

The Bloch equation (16) can also be used to generate the *linked-diagram expansion* [8, 9, 15, 16, 25]

$$[\Omega^{(n)}, H_0]P = (H'\Omega - \Omega P H'_{\text{eff}})^{(n)}_{\text{linked}}P, \quad (21)$$

where the subscript *linked* refers to linked diagrams, i.e., diagrams with no disconnected, closed part [16]. The last term on the right-hand side represents so-called *folded diagrams*, which appear only for open-shell states [57, 10].

## 2.2 Closed-shell states

For the rest of this paper we shall restrict ourselves to *closed-shell ground states*. (The treatment will be valid – with trivial modifications – also for systems with a single electron outside closed shells.) The target space then contains only a single wave function,  $\Psi$ , and the model space one model function,  $\Phi$ ,

$$H\Psi = E\Psi; \quad \Psi = \Omega\Phi; \quad H_0\Phi = E_0\Phi. \quad (22)$$

The model functions are projections onto the model space of the corresponding target functions, i.e., for a closed-shell system

$$\langle \Phi | \Psi \rangle = \langle \Phi | \Omega | \Phi \rangle = 1, \quad (23)$$

assuming the model function,  $\Phi$ , to be normalized to unity.

The Bloch equation (19), (21) assumes for closed-shell systems the simple form

$$[\Omega^{(n)}, H_0] | \Phi \rangle = (H' \Omega - \Omega P H' \Omega)^{(n)} | \Phi \rangle = Q(H' \Omega)_{\text{linked}}^{(n)} | \Phi \rangle, \quad (24)$$

where  $P = |\Phi\rangle\langle\Phi|$ .

Instead of an order-by-order expansion of the wave operator, we shall often use *successive approximations*,

$$\Omega_n = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots + \Omega^{(n)}, \quad (25)$$

so that  $\Omega_n \rightarrow \Omega$  as  $n \rightarrow \infty$ . These approximations can be obtained by solving the Bloch equation recursively,

$$\boxed{[\Omega_n, H_0] | \Phi \rangle = (H' \Omega - \Omega P H' \Omega)_n | \Phi \rangle = Q(H' \Omega)_{n, \text{linked}} | \Phi \rangle.} \quad (26)$$

Also the effective Hamiltonian contains only *linked* terms/diagrams and can be given the forms

$$H_{\text{eff}} = P(H \Omega)_{\text{linked}} P = P(H_0 + (H' \Omega)_{\text{linked}}) P = P(H + (H' \chi)_{\text{linked}}) P, \quad (27)$$

where we have introduced the *correlation operator* [16]

$$\chi = \Omega - 1. \quad (28)$$

The ground-state energy is according to (13)

$$E = \langle \Phi | H_{\text{eff}} | \Phi \rangle, \quad (29)$$

and using the successive approximations (25), the perturbative energy of order  $(n + 1)$  becomes

$$E_{n+1} = \langle \Phi | H_{\text{eff}, n+1} | \Phi \rangle. \quad (30)$$

## 2.3 Energy expectation value

The perturbative energy (30) is not variational, and in the following we shall therefore consider the corresponding *energy expectation value*,

$$\langle E \rangle_{n+1} = \frac{\langle \Psi_n | H | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \frac{\langle \Phi | \Omega_n^\dagger H \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle}, \quad (31)$$

which clearly has this property.

In any finite order the expectation value as well as the perturbative energy depends on the way the partitioning of the Hamiltonian (2) is performed – i.e., on the potential  $u$ . Since the expectation value is variational, it must have a minimum under the variation of the partitioning, and we shall now investigate the conditions for this minimum.

In order to simplify the expression above, we rewrite the numerator by means of the Bloch equation (26),

$$\Omega_n^\dagger H \Omega_n = \Omega_n^\dagger \Omega_n H_0 - \Omega_n^\dagger [\Omega_n, H_0] + \Omega_n^\dagger H' \Omega_n = \Omega_n^\dagger \Omega_n H_0 + \Omega_n^\dagger H' \Omega^{(n)} + \Omega_n^\dagger (\Omega P H' \Omega)_n, \quad (32)$$

where  $\Omega^{(n)} = \Omega_n - \Omega_{n-1}$ . After some algebra, one then finds that the expectation value (31) can be expressed

$$\boxed{\langle E \rangle_{n+1} = \frac{\langle \Phi | \Omega_n^\dagger H \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle} = \langle \Phi | H \Omega_n + \text{h.o.t.} | \Phi \rangle,} \quad (33)$$

where 'h.o.t.' stands for terms of order  $(n + 2)$  and higher. The r.h.s is – apart from the h.o.t. – identical to the corresponding perturbative energy (30), which verifies the expected result that the perturbative – or diagrammatic – expansion of the expectation value is up to order  $n + 1$  identical to that of the perturbative energy in intermediate normalization. In addition, the expectation value contains terms beyond order  $n + 1$ , which makes it variational. Of course, in the limit  $n \rightarrow \infty$  the two expansions will be identical. The expression  $H\Omega$  is not hermitean in intermediate normalization, but this is compensated for by the higher-order terms, so that the entire expression is hermitean.

We shall now investigate under what conditions the energy expectation value (31) is minimum, when the partitioning (2) or – equivalently – the potential  $u$  is varied. The minimum condition can be expressed

$$\delta\langle E\rangle_{n+1} = \delta\left(\frac{\langle\Phi|\Omega_n^\dagger H\Omega_n|\Phi\rangle}{\langle\Phi|\Omega_n^\dagger\Omega_n|\Phi\rangle}\right) = \delta\langle\Phi|H\Omega_n + \text{h.o.t.}|\Phi\rangle = 0, \quad (34)$$

where  $\delta$  represents any modification of the partitioning/potential.

We assume now that we modify the determinant  $\Phi$  by a small admixture of a *single substitution*,

$$\delta\Phi = \eta\Phi_a^r \quad (35)$$

and make the corresponding modification of the potential. Here,  $\Phi_a^r$  is the determinant  $\Phi$  with the occupied orbital  $a$  replaced by the unoccupied (or virtual) orbital  $r$ , and  $\eta$  is a small number. This corresponds to an orbital modification

$$\phi_a \rightarrow \phi_a + \eta\phi_r; \quad \phi_r \rightarrow \phi_r - \eta\phi_a. \quad (36)$$

The minimum condition (34) now becomes

$$\langle\delta\Phi|H\Omega_n + \text{h.o.t.}|\Phi\rangle + \langle\Phi|H\Omega_n + \text{h.o.t.}|\delta\Phi\rangle + \langle\Phi|H\delta\Omega_n + \text{h.o.t.}|\Phi\rangle = 0, \quad (37)$$

where the last term represents the effect of the corresponding modification of  $\Omega_n$ . These variations have to be made with some care. We are interested in the *change of the diagonal element* of the effective Hamiltonian, while in (37) also some undefined non-diagonal elements may seem to appear. In order to handle this subtle problem properly, we can think of replacing the effective Hamiltonian,  $H_{\text{eff}}$ , by a *reaction operator*,  $\mathcal{H}$ , which has the same *closed* part (operating within the model space) as  $H_{\text{eff}}$ ,

$$\langle\Phi|\mathcal{H}|\Phi\rangle = \langle\Phi|H_{\text{eff}}|\Phi\rangle, \quad (38)$$

but which also has an *open* part, operating outside this space. This part can be defined by means of *second quantization* [16]. In the effective Hamiltonian,  $H$  or  $H'$  operates on the wave operator, and all creation and annihilation operators must be completely contracted in order to contribute (in the closed-shell case). *The reaction operator is constructed in the same way as the effective Hamiltonian, but the operators need not be completely contracted.*

Obviously we must have  $\delta\langle\Phi|\chi|\Phi\rangle = 0$ , which yields a condition for  $\delta\chi = \delta\Omega$ ,

$$\langle\delta\Phi|\chi_n|\Phi\rangle + \langle\Phi|\chi_n|\delta\Phi\rangle + \langle\Phi|\delta\chi_n|\Phi\rangle = 0, \quad (39)$$

where the correlation operator,  $\chi$ , is given by (28). Similarly, we must have

$$\delta\langle\Phi|H_0\chi|\Phi\rangle = \delta\langle\Phi|\chi H_0|\Phi\rangle = 0,$$

which yields the only non-vanishing, non-diagonal elements of  $\delta H_0$ , i.e., the change in  $H_0$  due to the modification (35),

$$\langle\delta\Phi|\delta H_0|\Phi\rangle = \langle\Phi|\delta H_0|\delta\Phi\rangle = \eta^2(\varepsilon_a - \varepsilon_r). \quad (40)$$

When these relations are used in (37), one finds that the  $\delta\Omega_n$  contribution exactly cancels the  $H_0\chi_n$  part of the first two terms as well as the unlinked part of  $H\Omega_n$  that can be formed in these

terms when  $H'$  is operating on  $\Omega_n$  in second quantization. Since the wave operator is completely linked, we can then express the reaction operator as

$$\boxed{\mathcal{H}_{n+1} = (H\Omega_n)_{\text{linked}} = H_0 + (H'\Omega_n)_{\text{linked}} = H + (H'\chi_n)_{\text{linked}}} \quad (41)$$

and the condition that the energy expectation value,  $\langle E \rangle_{n+1}$ , is stationary for the substitution (35) as

$$\boxed{\langle \Phi_a^r | \mathcal{H}_{n+1} + \text{h.o.t.} | \Phi \rangle = 0.} \quad (42)$$

Here, all the forms of the reaction operator in (41) yield identical results.

At the global minimum of  $\langle E \rangle_{n+1}$ , the condition (42) must hold for all occupied orbitals  $a$  and all virtual orbitals  $r$ . In the following sections we shall investigate the consequences of this condition. As an introduction, we shall first consider the simple case of minimizing the first-order energy, which leads to the well-known Hartree-Fock equations. In the section thereafter we shall consider the minimization of the expectation value in arbitrary order and demonstrate that this leads in the limit  $n \rightarrow \infty$  to *Brueckner orbitals*.

### 3 First-order energy. Hartree-Fock

In this section we shall minimize the energy expectation value of a closed-shell system in first order (31), i.e., the expectation value of the Hamiltonian of the system,

$$\langle E \rangle_1 = \langle \Phi | H | \Phi \rangle. \quad (43)$$

This is stationary for single substitutions (35), if

$$\langle \Phi_a^r | H | \Phi \rangle = \langle \Phi_a^r | H' | \Phi \rangle = 0 \quad (44)$$

for all  $a$  and  $r$ , which is the *Hartree-Fock (HF) condition*. With the form (3) of the perturbation  $H'$ , the matrix element is here in the single-particle representation

$$\begin{aligned} \langle \Phi_a^r | H' | \Phi \rangle &= \langle \Phi_a^r | -\hat{U} + \hat{W} | \Phi \rangle = \langle r | -u | a \rangle + \sum_b^{\text{occ}} \left\langle r b \left| \frac{1 - P_{12}}{r_{12}} \right| a b \right\rangle = \\ &= \langle r | -u + \hat{v}_{\text{HF}} | a \rangle = \langle r | v_{\text{eff}} | a \rangle, \end{aligned} \quad (45)$$

where  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  is the interelectronic distance and  $P_{12}$  is the exchange operator.  $\hat{v}_{\text{HF}}$  is the *Hartree-Fock potential* with the matrix elements

$$\begin{aligned} \langle r | \hat{v}_{\text{HF}} | a \rangle &= \langle \Phi_a^r | \hat{W} | \Phi \rangle = \sum_b^{\text{occ}} \left\langle r b \left| \frac{1 - P_{12}}{r_{12}} \right| a b \right\rangle = \\ &= \sum_b^{\text{occ}} \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_r^*(\mathbf{r}_1) \phi_b^*(\mathbf{r}_2) \frac{1 - P_{12}}{r_{12}} \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2). \end{aligned} \quad (46)$$

$v_{\text{eff}}$  is referred to as the *effective potential* and defined by

$$v_{\text{eff}} = -u + \hat{v}_{\text{HF}}. \quad (47)$$

This potential can be represented graphically by the MBPT diagrams in Fig.1, where the last two diagrams represent the Hartree-Fock potential (46).

The minimum condition (44) can now be expressed

$$\langle \Phi_a^r | H | \Phi \rangle = \langle \Phi_a^r | \hat{T} + \hat{W} + \hat{V}_{\text{ext}} | \Phi \rangle = \langle r | -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) | a \rangle = 0 \quad (48)$$

for all occupied orbitals  $a$  and virtual orbitals  $r$ . Using the closure property, this can be written

$$\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) \right] | a \rangle - \sum_b^{\text{occ}} | b \rangle \langle b | \left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) \right] | a \rangle = 0, \quad (49)$$

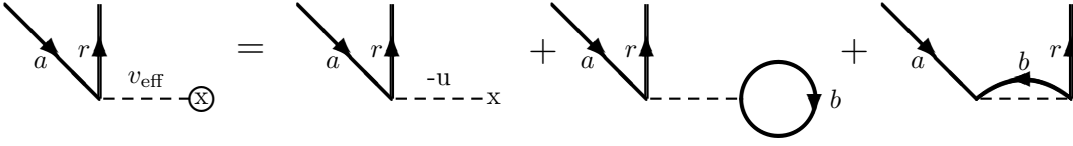


Figure 1: Graphical representation of the 'effective potential', defined in (47). The first diagram on the right-hand side represents the (negative) potential interaction in  $H'$  (3) and the last two diagrams the Hartree-Fock potential,  $\hat{v}_{\text{HF}}$  (46).

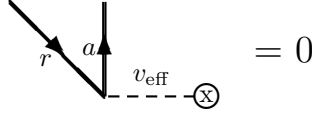


Figure 2: Graphical representation of the Brillouin theorem (52).

a relation that could also be obtained by minimizing the expression (43) with the ortho-normality constraint, using the Euler-Lagrange equation. The potential is here hermitean, and the equation can be expressed in canonical form

$$\left[ -\frac{1}{2}\nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) \right] |a\rangle = \varepsilon_a |a\rangle. \quad (50)$$

These are the *Hartree-Fock equations*. Comparing with the single-particle equations (6), we see that this corresponds to the potential

$$u = u_{\text{HF}} = \hat{v}_{\text{HF}} \quad (51)$$

in the zeroth-order Hamiltonian (3). The HF potential depends on the occupied orbitals, and the equations have to be solved *self-consistently*.

It follows from MBPT [16] that the first-order contribution to the wave function in the form of a single substitution,  $\Phi_a^r$ , is proportional to  $\langle \Phi_a^r | H' | \Phi \rangle$ . It then follows from (44) that there are *no single substitutions in the first-order Hartree-Fock wave function*, which is *Brillouin's theorem*. This theorem can also be expressed, using (45),

$$\langle r | v_{\text{eff}} | a \rangle = 0 \quad (52)$$

and illustrated as in Fig. 2.

The energy associated with an occupied orbital is in first order

$$e_a = \langle \Phi_a^a | H | \Phi \rangle, \quad (53)$$

which is evaluated in the same way as the matrix element in (48) but with  $r$  replaced by  $a$ . It then follows from (50) that this is equal to the orbital eigenvalue,

$$e_a = \langle a | -\frac{1}{2}\nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) | a \rangle = \varepsilon_a \quad (54)$$

which is *Koopmans' theorem*. Here, all other orbitals are unaffected, which means that *no relaxation effects* are included in this removal energy.

## 4 Higher-order energies. Brueckner orbitals

We shall now consider the energy expectation value in higher orders of perturbation theory – still restricting ourselves to the ground state of closed-shell systems – in order to find out under what conditions this will be stationary under the variation of the partitioning (2). We start with the second order, which we carry through in some detail, mainly for pedagogical reasons.



## 4.1 Second order

The second-order energy expectation value is according to (33)

$$\langle E \rangle_2 = \frac{\langle \Phi | \Omega_1^\dagger H \Omega_1 | \Phi \rangle}{\langle \Phi | \Omega_1^\dagger \Omega_1 | \Phi \rangle} = \langle \Phi | H \Omega_1 + \text{h.o.t.} | \Phi \rangle, \quad (55)$$

and the minimization leads to the condition (42)

$$\langle \Phi_a^r | \mathcal{H}_2 + \text{h.o.t.} | \Phi \rangle = \langle \Phi_a^r | H + (H' \Omega^{(1)})_{\text{linked}} + \text{h.o.t.} | \Phi \rangle = 0, \quad (56)$$

where  $\Omega^{(1)}$  is the first-order contribution to the wave operator (20). The first term of the second expression can as in the Hartree-Fock case (48) be represented by

$$\langle \Phi_a^r | H | \Phi \rangle = \langle r | -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{ext}}(\mathbf{r}) | a \rangle, \quad (57)$$

where  $\hat{v}_{\text{HF}}$  is the Hartree-Fock potential (46). The second term can be represented by means of a *second-order non-local correlation potential*

$$\langle \Phi_a^r | (H' \Omega^{(1)})_{\text{linked}} | \Phi \rangle = \sum_{\Phi^A \neq \Phi}^{\text{linked}} \frac{\langle \Phi_a^r | H' | \Phi^A \rangle \langle \Phi^A | H' | \Phi \rangle}{E_0 - E_0^A} = \langle r | \hat{v}_{\text{corr},2}^{\text{BO}} | a \rangle. \quad (58)$$

The minimum condition (56) then yields

$$\langle r | -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr},2}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) + \text{h.o.t.} | a \rangle = 0 \quad (59)$$

for all  $a$  and  $r$ , where 'h.o.t.' here represents a potential contribution due to the higher-order terms – in this case beyond second order. In analogy with (50) this yields

$$\left( -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr},2}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) + \text{h.o.t.} \right) \phi_a = \varepsilon_a \phi_a. \quad (60)$$

(Here, the potential is not necessarily hermitean, but we shall anyhow leave out possible off-diagonal multipliers, which will not be important for our discussions, and write the orbital equations in canonical form.) Comparing this equation with the zeroth-order Hamiltonian (3), we find that up to second order it corresponds to a potential

$$u = u_{\text{BO},2} = \hat{v}_{\text{HF}} + \hat{v}_{\text{corr},2}^{\text{BO}}. \quad (61)$$

At the global minimum of  $\langle E \rangle_2$  the equation (60) must be satisfied for all occupied orbitals.

It follows from MBPT [16] – and it will also be shown below (79) – that the first two terms of the second expression in (56) represent the amplitude of the admixture of the single substitution  $\Phi_a^r$  in the second-order wave function (apart an additional energy denominator). When this vanishes, the *Brillouin-Brueckner condition* [6] is satisfied to this order. This implies that the orbitals generated by the equations (60) with the higher-order terms removed,

$$\left( -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr},2}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) \right) \phi_a = \varepsilon_a \phi_a, \quad (62)$$

would be *second-order Brueckner orbitals* (BO). We shall now have a closer look upon these orbitals.

We shall first consider the correlation potential (58) and start with the corresponding energy expression (55),

$$E^{(2)} = \langle \Phi | (H' \Omega^{(1)})_{\text{linked}} | \Phi \rangle = \sum_{\Phi^A \neq \Phi}^{\text{linked}} \frac{\langle \Phi | H' | \Phi^A \rangle \langle \Phi^A | H' | \Phi \rangle}{E_0 - E_0^A}. \quad (63)$$

The intermediate states,  $\Phi^A$ , can here be singly or doubly excited,

$$E^{(2)} = \sum_{a,t}^{\text{linked}} \frac{\langle \Phi | H' | \Phi_a^t \rangle \langle \Phi_a^t | H' | \Phi \rangle}{\varepsilon_a - \varepsilon_t} + \sum_{ab,tu}^{\text{linked}} \frac{\langle \Phi | H' | \Phi_{ab}^{tu} \rangle \langle \Phi_{ab}^{tu} | H' | \Phi \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u}, \quad (64)$$

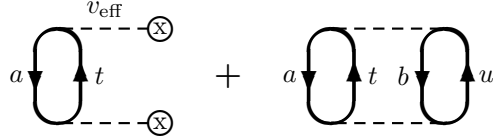


Figure 3: MBPT diagrams (of Goldstone type) representing the second-order contribution to the energy for a closed-shell system, leaving out the exchange variant. The graphical representation of the effective potential,  $v_{\text{eff}}$ , is given in Fig.1.

and this is represented by the linked many-body diagrams (of Goldstone type) [16] in Fig.3 (leaving out the exchange variant of the second diagram).

The graphical representation of the second-order correlation potential can easily be obtained by considering the definition of the reaction operator (38). As mentioned there, the effective Hamiltonian is in second-quantized form for a closed-shell system represented by fully contracted terms, i.e., by diagrams that are completely closed. The reaction operator is represented by the same second-quantized terms, but the terms need not be fully contracted. The diagrams of the reaction operator can therefore be obtained from those of the effective Hamiltonian by 'breaking up' the closed lines. The diagrams obtained in this way with a single pair of open lines, corresponding to single substitutions, are shown in Fig.4. The first four diagrams represent

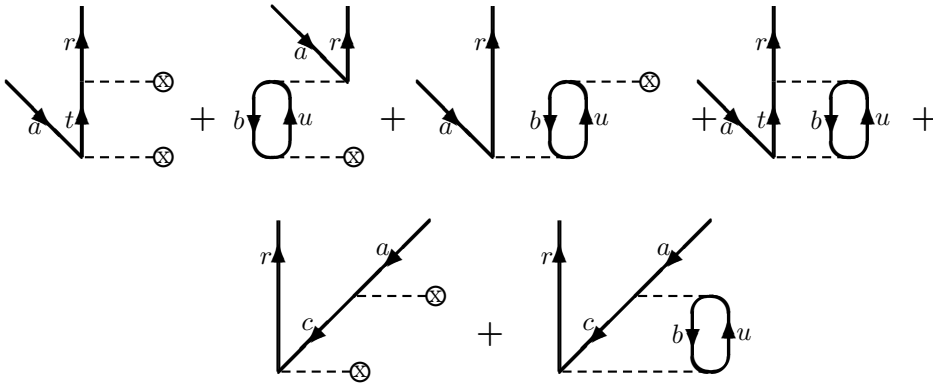


Figure 4: Diagrams representing the change in the second-order contribution to the energy due to the orbital modifications. These diagrams also represent the second-order correlation potential,  $v_{\text{corr},2}^{\text{BO}}$  (58). The first four diagrams represent correlation effects and the last two effects of the orbital relaxation. Exchange diagrams are left out.

*correlation effects* associated with the orbital  $a$  with the remaining occupied orbitals frozen, while the remaining two diagrams represent the effect due to the *relaxation* of the occupied orbitals. Together with the Hartree-Fock potential (last two diagrams in Fig.1) these diagrams represent the second-order Brueckner potential,  $u_{\text{BO},2}$  (61), appearing in the equation for the second-order Brueckner orbitals (62).

Next, we shall consider the significance of the orbital energies, which, using (62), are given by

$$\varepsilon_a = \langle a | -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr},2}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) | a \rangle. \quad (65)$$

The diagonal element of the correlation potential is not defined by the expression (58), but we shall make the natural extension and let this element be given by the same expression in the single-particle representation (or second quantization) as the non-diagonal element with  $r$  replaced by  $a$ . Formally, the diagonal element can be expressed

$$\langle a | \hat{v}_{\text{corr},2}^{\text{BO}} | a \rangle = \langle \Phi_a^a | (H' \Omega^{(1)})_{\text{linked}} | \Phi \rangle, \quad (66)$$

and, using (54), it then follows that the eigenvalue is given by

$$\varepsilon_a = \langle \Phi_a^a | H + (H' \Omega^{(1)})_{\text{linked}} | \Phi \rangle = \langle \Phi_a^a | \mathcal{H}_2 | \Phi \rangle, \quad (67)$$

which is equal to the energy associated with the orbital  $a$  or the negative of the corresponding ionization energy, including correlation and orbital relaxation effects to second order. This is a *generalization of Koopmans' theorem* in Hartree-Fock theory (54). The diagonal element of the correlation potential represents the effect of correlation and orbital relaxation. Diagrammatically, this part of the energy is represented by the same diagrams as the correlation potential shown above with the outgoing virtual orbital line  $r$  replaced by an outgoing occupied orbital line  $a$  (see further below).

## 4.2 All orders

We shall now minimize the energy expectation value in arbitrary order (33), (41),

$$\langle E \rangle_{n+1} = \frac{\langle \Phi | \Omega_n^\dagger H \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle} = \langle \Phi | \mathcal{H}_{n+1} + \text{h.o.t.} | \Phi \rangle = \langle \Phi | H + (H' \chi)_{n+1, \text{linked}} + \text{h.o.t.} | \Phi \rangle. \quad (68)$$

The condition for minimum is according to (42)

$$\langle \Phi_a^r | H + (H' \chi)_{n+1, \text{linked}} + \text{h.o.t.} | \Phi \rangle = \langle \Phi_a^r | H + \mathcal{H}_{\text{corr}, n+1} + \text{h.o.t.} | \Phi \rangle = 0, \quad (69)$$

where we have introduced the *correlation part* of the reaction operator,

$$\mathcal{H}_{\text{corr}} = \mathcal{H} - H = (H' \chi)_{\text{linked}}. \quad (70)$$

This condition leads in analogy with (59) to the equation

$$\langle \Phi_a^r | H + \mathcal{H}_{\text{corr}, n+1} + \text{h.o.t.} | \Phi \rangle = \langle r | -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}, n+1}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) + \text{h.o.t.} | a \rangle = 0 \quad (71)$$

and to the orbital equations

$$\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}, n+1}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) + \text{h.o.t.} \right] \phi_a = \varepsilon_a \phi_a, \quad (72)$$

where

$$\langle r | \hat{v}_{\text{corr}, n+1}^{\text{BO}} | a \rangle = \langle \Phi_a^r | \mathcal{H}_{\text{corr}, n+1} | \Phi \rangle \quad (73)$$

is the correlation potential of order  $(n+1)$ .

We shall show below that the orbitals generated by equation (72) – *with the higher-order terms removed*,

$$\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}, n+1}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) \right] \phi_a = \varepsilon_a \phi_a, \quad (74)$$

are *Brueckner orbitals* of order  $n+1$ . It is obvious that in the limit  $n \rightarrow \infty$  the two equations (72) and (74) become identical and equal to

$$\boxed{\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) \right] \phi_a = \varepsilon_a \phi_a,} \quad (75)$$

where the correlation potential (73) is

$$\langle r | \hat{v}_{\text{corr}}^{\text{BO}} | a \rangle = \lim_{n \rightarrow \infty} \langle r | \hat{v}_{\text{corr}, n+1}^{\text{BO}} | a \rangle = \langle \Phi_a^r | \mathcal{H}_{\text{corr}} | \Phi \rangle = \langle \Phi_a^r | (H' \chi)_{\text{linked}} | \Phi \rangle. \quad (76)$$

*This is the equation for all-order Brueckner orbitals.* We refer to the potential in this equation,

$$u_{\text{BO}} = \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}}^{\text{BO}}, \quad (77)$$

as the *Brueckner potential*. The correlation part of this potential is represented graphically by the second-order Goldstone diagrams in Fig. 4 together with all higher-order linked diagrams with a single pair of free orbital lines.

The Brueckner potential derived in intermediate normalization is not hermitean, and therefore the orbitals would not be automatically orthogonal. In order to generate orthonormal orbitals, the non-diagonal Lagrange multipliers, left out in the treatment above, should be maintained.

That the orbitals generated by the equation (74) are Brueckner orbitals of a certain order can be shown in the following way. From the Bloch equation in linked-diagram form for a closed-shell system (26),

$$[\Omega_n, H_0]|\Phi\rangle = (QH'\Omega)_{n,\text{linked}}|\Phi\rangle, \quad (78)$$

we obtain by operating with  $\langle\Phi_a^r|$  from the left

$$(\varepsilon_a - \varepsilon_r)\langle\Phi_a^r|\Omega_n|\Phi\rangle = \langle\Phi_a^r|(H'\Omega)_{n,\text{linked}}|\Phi\rangle, \quad (79)$$

where  $\varepsilon_r - \varepsilon_a$  is the excitation energy of  $\Phi_a^r$ . The matrix element on the left-hand side,  $\langle\Phi_a^r|\Omega_n|\Phi\rangle = \langle\Phi_a^r|\Psi_n\rangle$ , represents the coefficient for  $\Phi_a^r$  in the  $n$ :th-order wave function,  $\Psi_n$ . Therefore, if we have

$$\langle\Phi_a^r|\Omega_n|\Phi\rangle = \langle\Phi_a^r|\Psi_n\rangle = 0 \quad (80)$$

for all occupied orbitals  $a$  and all virtual orbitals  $r$ , then there would be no singles in the  $n$ :th-order wave function. This is the *Brillouin-Brueckner* condition, which is equivalent to

$$\boxed{\langle\Phi_a^r|\mathcal{H}_n|\Phi\rangle = \langle\Phi_a^r|(H'\Omega)_{n,\text{linked}}|\Phi\rangle = 0.} \quad (81)$$

With  $n \rightarrow n + 1$  this becomes identical to the condition (69), apart from the higher-order terms. This implies that with orbitals that are solutions of the equations (74) there are no single substitutions in the wave function of order  $(n + 1)$ , and hence the orbitals are *Brueckner orbitals of this order*. Eq. (80) is also the condition for *maximum overlap* between the zeroth-order determinant and the correlated wave function, which is another criteria for BO.

The Brillouin-Brueckner condition of a certain order (81) can be represented graphically by *all linked diagrams* up to this order with a single pair of free lines, as shown schematically in Fig. 5. The diagrams are here identical to those of the BO potential of the same order with the addition of the diagram for  $-u$  (see Fig. 1).

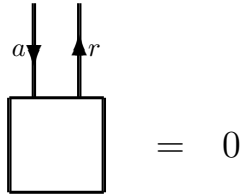


Figure 5: Graphical representation of the generalized Brillouin-Brueckner theorem (81). The graphical symbol represents all closed and linked MBPT diagram with no other free lines that those explicitly shown. For the two lowest orders the corresponding diagrams are given in Figs 1 and 4.

The significance of the Brueckner orbital energy of arbitrary order can be shown in the same way as in second order. The energy associated with an occupied orbital in  $n$ :th order is

$$e_a = \langle\Phi_a^a|\mathcal{H}_n|\Phi\rangle, \quad (82)$$

evaluated in analogy with (66). In all orders this becomes

$$e_a = \langle\Phi_a^a|H_0 + (H'\Omega)_{\text{linked}}|\Phi\rangle = \langle\Phi_a^a|H_0 + H' + (H'\chi)_{\text{linked}}|\Phi\rangle, \quad (83)$$

using (41), and if we define the diagonal elements of the correlation potential in analogy with (66) this can be expressed

$$e_a = \varepsilon_a + \langle a|v_{\text{eff}} + \hat{v}_{\text{corr}}^{\text{BO}}|a\rangle = \varepsilon_a + \langle a|u_{\text{BO}} - u|a\rangle, \quad (84)$$

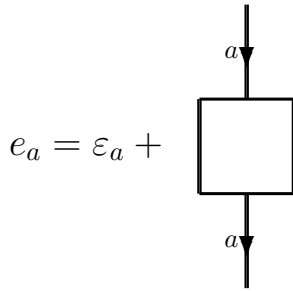


Figure 6: Graphical representation of (the negative of) the electron binding energy or ionization energy. The box is the same as in Fig. 5 and the diagrams represent the correction to the orbital energy eigenvalue. When the orbitals are Brueckner orbitals, these diagrams vanish in the same way as in Fig. 5.

using (45) and (76). Here,  $u_{\text{BO}}$  is the Brueckner potential (77) and  $u$  is the potential in the zeroth-order Hamiltonian (3). This is a general relation between the orbital energy eigenvalue and (the negative of) the electron binding energy and represented graphically as shown in Fig. 6. The box is here the same as in Fig. 5. When the orbitals are Brueckner orbitals, the second term in (84) and the diagrams in this figure vanish. We then find that the energy eigenvalues of an occupied Brueckner orbital is equal to the negative of the corresponding ionization energy,

$$\boxed{e_a = \epsilon_a}. \quad (85)$$

This includes correlation and orbital-relaxation effects to all orders of perturbation theory. This is the *generalized Koopmans' theorem* (54). This result has been confirmed by accurate numerical calculations [52].

In summary, we have shown that *minimizing the energy expectation value of a closed-shell system in a certain order of perturbation theory,*

$$\langle E \rangle_{n+1} = \frac{\langle \Psi_n | H | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \frac{\langle \Phi | \Omega_n^\dagger H \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle}, \quad (86)$$

*by varying the partitioning of the Hamiltonian, leads to orbitals that approach Brueckner orbitals as the order of perturbation increases.*

Furthermore, we have shown that *the energy eigenvalues of the occupied Brueckner orbitals are equal to the negative of the corresponding electron binding energies, including relaxation and correlation effects to all orders. This is the generalized Koopmans' theorem.*

## 5 Density-functional procedures

We shall now compare the MBPT discussed above with the density-functional theory (DFT). We shall start by deriving the standard Kohn-Sham scheme, using the Levy constrained search [32] and the so-called Hartree-Fock-Kohn-Sham scheme of Seidl, Görling et al. [49]. Finally we shall extend this procedure and propose a new scheme, referred to as the *Brueckner-Kohn-Sham scheme*, where also electron correlation is introduced into the model. It will be shown that this leads to a *non-local exchange-correlation potential*, and it will be argued that the orbitals of this model are essentially *Brueckner orbitals*.

## 5.1 Standard Kohn-Sham model

In the constrained-search formalism the Hohenberg-Kohn energy functional for an *interacting*  $N$ -electron system is

$$E_{\text{HK}}[\rho] = F_{\text{HK}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}), \quad (87)$$

where

$$F_{\text{HK}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle = T_{\text{HK}}[\rho] + W_{\text{HK}}[\rho] \quad (88)$$

is the *universal Hohenberg-Kohn functional* and  $v_{\text{ext}}(\mathbf{r})$  is the (local) external potential.  $\hat{T}$  and  $\hat{W}$  are the kinetic-energy and the electron-electron-interaction operators, respectively (1). The electron-electron-interaction functional  $W_{\text{HK}}[\rho]$  can be separated into

$$W_{\text{HK}}[\rho] = J[\rho] + E_{\text{xc}}^{\text{HK}}[\rho], \quad (89)$$

where

$$J[\rho] = \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (90)$$

is the Coulomb interaction (Hartree) functional and  $E_{\text{xc}}^{\text{HK}}[\rho]$  the universal Hohenberg-Kohn exchange-correlation energy functional.

Minimizing the HK energy functional with respect to the electron density, keeping the total electronic charge constant, leads to the *exact ground-state energy*,

$$\min_{\rho} E_{\text{HK}}[\rho] = E_{\text{HK}}[\rho_0] = E_{\text{ground state}}, \quad (91)$$

where  $\rho_0$  is the *exact ground-state density*.

In the *standard Kohn-Sham model* the interacting system is replaced by a system of *non-interacting electrons*, moving in a *local potential*,  $v_{\text{KS}}(\mathbf{r})$ ,

$$H_{\text{KS}} = \hat{T} + \hat{V}_{\text{ext}} = \sum_{i=1}^N \left[ -\frac{1}{2} \nabla_i^2 + v_{\text{KS}}(\mathbf{r}_i) \right], \quad (92)$$

with the eigenstates given in the form of single-determinantal wave functions (5).

The Kohn-Sham kinetic-energy functional is according to the constrained search the *minimum of the kinetic energy for all determinants yielding a certain density*,  $\rho(\mathbf{r})$ ,

$$F_{\text{KS}}[\rho] = T_{\text{KS}}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle. \quad (93)$$

$T_{\text{KS}}$  is an (implicit) functional of the density but different from  $T_{\text{HK}}[\rho]$  in (88),

$$\Delta T_{\text{KS}}[\rho] = T_{\text{HK}}[\rho] - T_{\text{KS}}[\rho]. \quad (94)$$

Minimizing the kinetic energy (93) for a certain  $\rho(\mathbf{r})$ , leads to the Euler equation

$$\delta \left[ \langle \Phi | \hat{T} | \Phi \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{eff}}^{\text{KS}}(\mathbf{r}) \right] = 0, \quad (95)$$

where  $v_{\text{eff}}^{\text{KS}}(\mathbf{r})$  is a *Lagrangian multiplier function*. We can vary the orbitals of the Kohn-Sham wave function (5) and include also the Lagrangian multipliers for the ortho-normality constraint,

$$\frac{\delta}{\delta \phi_a^*} \left[ \langle \Phi | \hat{T} | \Phi \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{eff}}^{\text{KS}}(\mathbf{r}) - \sum_{a,b}^{\text{occ}} \varepsilon_{a,b} \langle a | b \rangle \right] = 0. \quad (96)$$

Alternatively, we can as before (35) include small components of single-substitutions, which yields

$$\langle \Phi_a^r | \hat{T} | \Phi \rangle + \langle r | v_{\text{eff}}^{\text{KS}}(\mathbf{r}) | a \rangle = 0. \quad (97)$$

Omitting any off-diagonal multipliers, we obtain the standard *Kohn-Sham equations*

$$\boxed{\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r})\right]|a\rangle = \varepsilon_a|a\rangle,} \quad (98)$$

where  $v_{\text{KS}}(\mathbf{r})$  is the *local Kohn-Sham potential* (92) and identical to the Lagrangian multiplier function  $v_{\text{eff}}^{\text{KS}}(\mathbf{r})$ .

The Kohn-Sham energy functional is

$$E_{\text{KS}}[\rho] = T_{\text{KS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{KS}}(\mathbf{r}), \quad (99)$$

and minimizing this functional with respect to the density under the constraint  $\int d\mathbf{r} \rho(\mathbf{r}) = N$ , leads to the Euler equation

$$\mu = \frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{KS}}(\mathbf{r}). \quad (100)$$

The Hohenberg-Kohn energy functional (87) can be expressed in terms of the Kohn-Sham kinetic-energy functional as

$$E_{\text{HK}}[\rho] = T_{\text{HK}}[\rho] + J[\rho] + E_{\text{xc}}^{\text{HK}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) = T_{\text{KS}}[\rho] + V_{\text{KS}}[\rho], \quad (101)$$

where

$$V_{\text{KS}}[\rho] = J[\rho] + E_{\text{xc}}^{\text{HK}}[\rho] + \Delta T_{\text{KS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}). \quad (102)$$

Minimizing this functional leads to the Euler equation

$$\mu = \frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (103)$$

We then see that this is the same as that of the independent-particle KS model (100) with

$$v_{\text{KS}}(\mathbf{r}) = \frac{\delta V_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\text{xc}}^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}), \quad (104)$$

where

$$E_{\text{xc}}^{\text{KS}}[\rho] = E_{\text{xc}}^{\text{HK}}[\rho] + \Delta T_{\text{KS}}[\rho]$$

is the exchange-correlation functional, including the kinetic-energy difference (94). This can also be expressed

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{Coul}}(\mathbf{r}) + v_{\text{xc}}^{\text{KS}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}), \quad (105)$$

where  $v_{\text{Coul}}$  is the Coulomb (Hartree) potential

$$v_{\text{Coul}}(\mathbf{r}) = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (106)$$

and  $v_{\text{xc}}^{\text{KS}}(\mathbf{r})$  is the *local Kohn-Sham exchange-correlation potential* (including a correction due to the kinetic-energy difference),

$$\boxed{v_{\text{xc}}^{\text{KS}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})}.} \quad (107)$$

When the Kohn-Sham equations (98) are solved self-consistently with the potential above, the exact ground-state electron density is generated and the energy functional (99) is minimized. This implies that, *if the exact potential can be found, the Kohn-Sham model yields the exact ground-state density and the exact ground-state energy of the system.*

## 5.2 Including electron exchange: Hartree-Fock–Kohn-Sham

Instead of minimizing only the kinetic energy for a constant electron density, as in the standard Kohn-Sham model (93), we could minimize the kinetic energy together with the electron-electron interaction – or part thereof – schemes known as *hybrid schemes* [50] or *generalized Kohn-Sham schemes* [49]. As an illustration, we consider a scheme where the entire interaction  $W$  (as in the Hartree-Fock scheme) is included, which leads to a model known as the *Hartree-Fock–Kohn-Sham (HF-KS) model*. The KS functional (93) is here replaced by

$$\begin{aligned} F_{\text{HFKS}}[\rho] &= \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} + \hat{W} | \Phi \rangle = \min_{\Phi \rightarrow \rho} \left\{ \langle \Phi | \hat{T} | \Phi \rangle + J[\rho] + E_{\text{ex}}^{\text{HF}}[\{\phi_i\}] \right\} = \\ &= T_{\text{HFKS}}[\rho] + J[\rho] + E_{\text{ex}}^{\text{HFKS}}[\rho]. \end{aligned} \quad (108)$$

Here, the minimization yields

$$\delta \left\{ \langle \Phi | \hat{T} | \Phi \rangle + J[\rho] + E_{\text{ex}}^{\text{HF}}[\{\phi_i\}] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{eff}}^{\text{HFKS}}(\mathbf{r}) \right\} = 0, \quad (109)$$

where  $v_{\text{eff}}^{\text{HFKS}}(\mathbf{r})$  is another (local) Lagrange multiplier function. This leads in the same way as before (96)-(98) to the canonical equations

$$\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{eff}}^{\text{HFKS}}(\mathbf{r}) \right] |a\rangle = \varepsilon_a |a\rangle, \quad (110)$$

where

$$\hat{v}_{\text{HF}} = v_{\text{Coul}}(\mathbf{r}) + \hat{v}_{\text{ex}}^{\text{HF}} \quad (111)$$

is the standard *non-local* HF potential (46) with the direct (Coulomb or Hartree) part and the exchange part.

The energy functional of the present scheme is

$$E_{\text{HFKS}}[\rho] = F_{\text{HFKS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{eff}}^{\text{HFKS}}(\mathbf{r}), \quad (112)$$

and minimization with respect to the density leads to the Euler equation

$$\mu = \frac{\delta F_{\text{HFKS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{eff}}^{\text{HFKS}}(\mathbf{r}). \quad (113)$$

As before, we compare with the HK energy functional (87), which we express as

$$E_{\text{HK}}[\rho] = F_{\text{HFKS}}[\rho] + E_{\text{corr}}^{\text{HFKS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}), \quad (114)$$

where

$$E_{\text{corr}}^{\text{HFKS}}[\rho] = E_{\text{xc}}^{\text{HK}}[\rho] - E_{\text{ex}}^{\text{HFKS}}[\rho] + T_{\text{HK}}[\rho] - T_{\text{HFKS}}[\rho] \quad (115)$$

is the correlation-energy functional including the differences between the kinetic-energy and exchange-interaction functionals of the two models. The Euler equation then becomes

$$\begin{aligned} \mu &= \frac{\delta F_{\text{HFKS}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\text{corr}}^{\text{HFKS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \\ &= \frac{\delta F_{\text{HFKS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{corr}}^{\text{HFKS}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}), \end{aligned} \quad (116)$$

and we find that this is the same as that of the HF-KS model (113) with

$$v_{\text{eff}}^{\text{HFKS}}(\mathbf{r}) = v_{\text{corr}}^{\text{HFKS}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}). \quad (117)$$

$v_{\text{corr}}^{\text{HFKS}}(\mathbf{r})$  is a *local, effective correlation potential*, including a correction due to the kinetic-energy and exchange differences. The equations for the orbitals then become

$$\boxed{\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + v_{\text{corr}}^{\text{HFKS}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \right] |a\rangle = \varepsilon_a |a\rangle.} \quad (118)$$



This can be regarded as *generalized Hartree-Fock equations* with an additional *local* correlation potential,  $v_{\text{corr}}^{\text{HFKS}}(\mathbf{r})$ , and is referred to as the *Hartree-Fock-Kohn-Sham scheme (HF-KS)* by Seidl, Görling et al. [49].

If the correlation potential,  $v_{\text{corr}}^{\text{HFKS}}$ , were known, solving the equations (118) self-consistently would lead to the *exact ground-state electron density* and the *exact ground-state energy*.

### 5.3 Including exchange-correlation: Brueckner-Kohn-Sham

In the Hartree-Fock-Kohn-Sham scheme considered above the electron exchange is included in the minimizing functional (108). We shall now extend this model by including also *electron correlation* into the model – not just in terms of a local potential – and we shall do this by a rather straightforward extension of the procedure in refs [49, 50]. This will be done in close analogy with the treatment of the energy expectation value and the *Brueckner orbitals* in the first part of the present paper. This leads to a scheme, which we refer to as the *Brueckner-Kohn-Sham (BKS) scheme*, which contains, as we believe, the maximum of correlation that can be included in a Kohn-Sham-like model. It will be argued that the orbitals generated in such a scheme would be essentially Brueckner orbitals. From this we shall draw some conclusions also about the orbitals of the standard Kohn-Sham and related schemes.

#### 5.3.1 Generalized Kohn-Sham model

We start with a general functional of the electron density,  $F_{\text{GKS}}[\rho]$ , which may also include electron correlation. Based upon that functional, we construct an independent-particle model, where the electrons move independently of each other in a potential due to this functional and an additional external *local* field  $v_{\text{GKS}}(\mathbf{r})$ . This corresponds to the energy functional

$$E_{\text{GKS}}[\rho] = F_{\text{GKS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{GKS}}(\mathbf{r}). \quad (119)$$

Minimizing this functional with respect to the electron density – keeping the total electron charge,  $\int d\mathbf{r} \rho(\mathbf{r}) = N$ , constant – leads to the Euler equation

$$\mu = \frac{\delta F_{\text{GKS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{GKS}}(\mathbf{r}). \quad (120)$$

Minimizing the universal Hohenberg-Kohn functional (88) with respect to the density, gives

$$\mu = \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}), \quad (121)$$

and this is the same equation as for the GKS model, if we set

$$\boxed{v_{\text{GKS}}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} (F_{\text{HK}}[\rho] - F_{\text{GKS}}[\rho]) + v_{\text{ext}}(\mathbf{r})}. \quad (122)$$

(This relation is identical to those in Eq. (9) of ref. [50] and Eq. (2.14) of ref. [49].) Applying this to the models discussed previously, we find that for the Kohn-Sham model

$$v_{\text{KS}}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} \left( J[\rho] + E_{\text{xc}}^{\text{HK}}[\rho] + \Delta T_{\text{KS}}[\rho] \right) + v_{\text{ext}}(\mathbf{r}) \quad (123)$$

with the notations used above, and for the Hartree-Fock-Kohn-Sham model

$$v_{\text{HFKS}}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} \left( E_{\text{corr}}^{\text{HK}}[\rho] + \Delta T_{\text{HFKS}}[\rho] + \Delta E_{\text{ex}}^{\text{HFKS}}[\rho] \right) + v_{\text{ext}}(\mathbf{r}), \quad (124)$$

where  $E_{\text{corr}}^{\text{HK}}[\rho]$  is the correlation part of the HK exchange-correlation functional and the next two terms represent the difference between the kinetic-energy and the exchange-interaction functionals of the HK and HFKS models.

The resulting orbital equations are obtained by minimizing the  $F$  functional with respect to the determinant  $\Phi$  and including the local potential  $v_{\text{GKS}}(\mathbf{r})$ .

### 5.3.2 Brueckner–Kohn–Sham

We shall now propose a scheme, which includes electron correlation as well as electron exchange in the non-local potential. This will be based upon the functional

$$F_{\text{BKS}}[\rho] = \min_{\Psi_n \rightarrow \rho} \frac{\langle \Psi_n | \hat{T} + \hat{W} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \min_{(\Omega_n \Phi) \rightarrow \rho} \frac{\langle \Phi | \Omega_n^\dagger (\hat{T} + \hat{W}) \Omega_n | \Phi \rangle}{\langle \Phi | \Omega_n^\dagger \Omega_n | \Phi \rangle}, \quad (125)$$

and we shall refer to this as the *Brueckner-Kohn-Sham* (BKS) scheme. Here,  $\Psi_n = \Omega_n \Phi$  is the  $n$ :th-order approximation of the wave function, where  $\Phi$  is as before a single Slater determinant and  $\Omega_n$  is the  $n$ :th-order wave operator (26). Since  $\Psi_n$  is not normalized in the intermediate normalization, we divide by the norm. We see that the expression in this functional is closely related to the energy expectation value (31) – we simply have to subtract the effect of the external field –

$$\frac{\langle \Psi_n | \hat{V}_{\text{ext}} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}), \quad (126)$$

giving

$$F_{\text{BKS}}[\rho] = \min_{(\Omega_n \Phi) \rightarrow \rho} \left[ \langle E \rangle_{n+1} - \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right]. \quad (127)$$

Using the identity (33), this can be expressed

$$F_{\text{BKS}}[\rho] = \min_{(\Omega_n \Phi) \rightarrow \rho} \left[ \langle \Phi | \mathcal{H}_{n+1} + \text{h.o.t.} | \Phi \rangle - \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right]. \quad (128)$$

As we have seen above, minimizing  $\langle E \rangle_{n+1}$  *without* the constraint, leads, in the limit  $n \rightarrow \infty$  to *Brueckner orbitals*. We shall now investigate the properties of the entire functional *with* the constraint.

The functional (125) is quite similar to the HK functional (88), the main difference being that the search in (125) is more restricted. The function  $\Psi_n = \Omega_n \Phi$  is *v-representable* [32, 33], which the function  $\Psi$  in the HK functional need not be. Therefore the functionals are (slightly) different.

From the relation (122) we obtain the local potential of the BKS model

$$v_{\text{BKS}}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} \left( F_{\text{HK}}[\rho] - F_{\text{BKS}}[\rho] \right) + v_{\text{ext}}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} \left( \Delta T_{\text{BKS}}[\rho] + \Delta E_{\text{xc}}[\rho] \right) + v_{\text{ext}}(\mathbf{r}), \quad (129)$$

where the first part is due to the differences between the kinetic energy and exchange-correlation functionals of the two models.

The orbital equations of the BKS model are obtained by minimizing the functional  $F_{\text{BKS}}[\rho]$  in analogy with (96)-(98). If the density in (126) were associated with the function  $\Phi$ , then that term would yield a potential that cancels  $v_{\text{ext}}$  in (129). Since the density in (126) is associated with the function  $\Omega_n \Phi$  rather than with  $\Phi$ , the cancellation is not complete. However, as the process converges, these densities will become more and more equal, and we can omit the potential difference. In the limit  $n \rightarrow \infty$  the orbital equations of the BKS model would then be

$$\left[ -\frac{1}{2} \nabla^2 + \hat{v}_{\text{HF}} + \hat{v}_{\text{corr}}^{\text{BO}} + v_{\text{ext}}(\mathbf{r}) + \delta v_{\text{F}}(\mathbf{r}) \right] |a\rangle = \varepsilon_a |a\rangle, \quad (130)$$

where  $\delta v_{\text{F}}(\mathbf{r})$  is the *local* correction potential in (129). These equations are identical to those of the Brueckner orbitals (75), apart from this correction. We believe that the kinetic-energy

difference is here even smaller than in the KS and HFKS models discussed above, since the functionals are generally more similar, and for the same reason we expect the difference between the exchange-correlation energy functionals to be quite small. *It would then follow that the orbitals of the BKS model are essentially Brueckner orbitals.*

## 6 Discussions and Conclusions.

In the generalized Kohn-Sham model introduced here, the *Brueckner-Kohn-Sham* (BKS) procedure, we start from a functional (125), which is as close as possible to the exact Hohenberg-Kohn functional. When the KKS functional is minimized without any restriction, it generates in the limit  $n \rightarrow \infty$  the exact energy and Brueckner orbitals. When used in a Kohn-Sham-like procedure, the BKS scheme yields an additional local potential term,  $\delta v_F(\mathbf{r})$ , which makes the orbitals generate the exact density. It is well-known that Brueckner orbitals usually reproduce the exact density quite well, and, therefore, there are strong reasons to believe that the potential correction has only a minor effect and that the orbitals of the BKS scheme actually are very close to Brueckner orbitals.

The BKS scheme represents in a way the ultimate scheme of the generalized Kohn-Sham type, and the standard Kohn-Sham (KS) scheme as well as the Hartree-Fock-Kohn-Sham (HF-KS) scheme can be regarded as special cases of this scheme. In the KS scheme only the kinetic energy is used in the first minimizing step, which leads to a local exchange-correlation potential. In the HF-KS scheme also the electron-exchange interaction is included in the first step, which leads to a non-local exchange potential of Hartree-Fock type and a local correlation potential. In the BKS scheme, finally, also the electron correlation is included in the first step, and this leads to a non-local exchange-correlation potential. We summarize this hierarchy of schemes in the box below:

*Standard Kohn-Sham: local exchange-correlation potential*  
*Hartree-Fock-Kohn-Sham: non-local exchange potential, local correlation potential*  
*Brueckner-Kohn-Sham: non-local exchange-correlation potential.*

We believe, as mentioned, that the BKS scheme generates orbitals that are very close to Brueckner orbitals. We also believe that other schemes, such as the standard Kohn-Sham scheme, generate orbitals that are close to Brueckner orbitals – closer than to Hartree-Fock orbitals – for the following reasons.

The HF exchange potential is completely delocalized. For physical reasons, however, one would expect the electrons to interact more strongly with electrons in the vicinity, and this would lead to a more 'localized' exchange potential, such as, for instance, the *screened exchange* potential, which has been suggested and applied by a number of authors [49, 58, 59, 60, 61, 62, 63]. In reality there exists no isolated exchange interaction – only the exchange-correlation has physical significance. It can be expected that the correlation has the effect of 'screening' the exchange, so that a screened exchange potential would automatically include some correlation effect. The Brueckner potential, which has a non-local exchange-correlation part, is likely to be 'more localized' than the HF exchange potential, and we believe that it represents a more 'physical' potential than does the HF potential. This might be the underlying reason why local potential approximations work as well as they do – from the original Slater approximation to the Kohn-Sham scheme – in many cases considerably better than the HF potential. This would indicate that the local potential approximations are in some sense closer to the non-local BO potential than to the completely delocalized HF potential, and that the orbitals generated by the local approximations are closer to the BO than to the HF orbitals. This is supported by early observations that results obtained with local exchange potentials often agree better with the Brueckner-orbital result than with the HF result [51].

It is well-known that the Brueckner orbitals do have definite physical significance in that the orbital energies represent closely the ionization energies and that other single-electron properties, such as the hyperfine interaction or the dipole moments, are well reproduced by such orbitals [51, 52, 53, 54]. This supports the recent observations that the Kohn-Sham orbitals and the orbital energies do have physical significance, contrary to what was originally anticipated. This is expected to be the case for the KS orbitals but even more so for the so-called hybrid schemes with partly non-local potential. It may be true to some extent also for orbitals generated by the local approximations of Slater type.

The exact form of the exchange-correlation potential in the Brueckner-Kohn-Sham scheme can at present be obtained only by elaborate many-body calculations. The intention here, however, has not been to construct a practical computational scheme but rather to shed some light onto the more traditional schemes. The Brueckner orbitals and the BKS potential have then been used as tools for this purpose. It may be possible, though, to find practically useful approximations of the BKS potential, for instance, by a screened exchange, for which the degree of screening could be determined by comparing with the Brueckner potential, obtained by means of MBPT.

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