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Two electrons in an external oscillator potential: exact solution versus one-particle approximations

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Received 9 January 1998

Abstract. We use the two-electron oscillator (with Coulomb interaction between the electrons) as a test system for a selection of the most common one-particle approximations: Hartree–Fock (HF), local spin density approximation (LSDA), with self-interaction correction (SIC), generalized gradient correction (GGA) and corrections for excitation energies. Moreover we compared excitation energies from total energy differences with the concept of the Slater transition state (STS) and with the difference of approximate and exact Kohn–Sham energies. By tuning the external oscillator frequency, one can realize the strong, intermediate and weak correlation regime within one system. The results are compared with exact charge densities, Kohn–Sham potentials, ground-state energies and excitation energies. Unlike previous papers on this model, we used self-consistent (and not the exact) charge densities as input for the density functional theory, which makes it possible to check the accuracy of the approximated density itself. We found that the LSDA describes the charge density even in the Wigner crystal limit qualitatively correct, although only SIC provides quantitatively satisfactory results. For *all* oscillator frequencies, the spurious wiggles in the GGA exchange potential are located near the classical turning point suggesting that they are a consequence of the divergence of the underlying Kirshnitz expansion in this region. It is also observed that the well known large error in the LSDA and GGA exchange potential is not present in self-interaction free methods such as HF and SIC giving rise to the assumption that self-interaction is responsible for this defect. KS eigenvalue differences (as zeroth approximations for excitation energies) calculated from the exact and LSDA effective potential are very close. Therefore, their common large difference with the exact excitation energies cannot be fixed by nonlocal corrections to the LSDA.

1. Introduction

The aim of theoretical physics is to develop and check basic notions in qualitative or exact mathematical form. One of those notions in the theory of the electronic structure of atoms, molecules and solids is the one-particle picture with implementations of Hartree–Fock (HF) theory, density functional theory (DFT), etc. These basic pictures can be checked by application to real physical systems and comparison with experiments, or by application to exactly solvable models and comparison with those results. The first approach has the advantage that one is concerned directly with the ultimate subject of research, namely nature. The problem is that one can measure only part of the physical information on the system, the numerical analysis is complicated, and the experimental results are often influenced by side effects. In the second approach one (often) has all of the information available, but the model might show simplifying features which cannot be found in real systems.

We investigate the simplest system which has Coulomb correlations in it, namely two electrons interacting via Coulomb interaction and subject to an external oscillator potential. This model is interesting for nuclear, atomic and solid-state physics alike. It has been known for a long time that it can be solved exactly in the sense that the Schrödinger equation decouples completely and the only new ordinary differential equation can be solved numerically. Recently however, it has been found that this remaining equation can also be solved analytically for a countably infinite set of oscillator frequencies [1]. The corresponding solutions have the form of a finite polynomial multiplied by an exponential function. This holds for ground and excited states as well as for singlet and triplet states. This model is a realistic picture as to the electron–electron interaction, but does not show the cusp originating in the singularity of external Coulomb potentials. The fact, however, that it has a free parameter (external oscillator frequency ω) allows us to tune the system between weakly and strongly correlated regimes, i.e. the independent particle and the Wigner crystal limit (in a finite and inhomogeneous system, though). The homogeneous electron gas and the Hubbard model are other model systems of this kind. It is hard to find a single *natural* system which allows us to tune the system similarly. Mostly one has to study both limiting cases in different systems.

One aim of this paper is to investigate how the results of typical one-particle theories can be mapped to the exact many-body processes and how precise these approximate treatments are. The approximations taken into account comprise the following: local spin density approximation (LSDA) (with homogeneous electron gas data from [2]) with and without self-interaction correction (SIC) [2] and the latest version of the generalized gradient approximation (GGA) [3], as well as HF and optimized effective potential (OEP) methods [5], whereby the latter two are identical in the singlet ground state of a two-electron system. As for the excitation energies, we also test the Slater transition state (STS), a recently published treatment by Petersilka, Gossmann and Gross (PGG) [6], who defined the excitation energies by means of the poles of the linear response function, and the formalism by Görling [7]. Since for our model system the *exact* effective Kohn–Sham (KS) potential is known [10–12], we also calculate the excited states in this potential. This gives additional information concerning the question of whether nonlocal corrections to the LSDA or the integer discontinuity of the effective potential is more important for excitation energies. Another question on which attention is focused is, how does DFT in the description of the strong correlation (low density or Wigner crystal) limit? Although our model is finite, it exhibits all the physics of electron localization (Wigner crystallization). Finally, we compare the above-mentioned results with an approximation within the many-body treatment, which is particularly suited for the strong correlation limit [1].

Similar investigations have been published previously [9–14]. The progress in this paper comprises the following elements: using the self-consistent density (and not the exact one) for the one-particle approximations, extension and refinement of the grid of ω values (including the regime of Wigner crystallization), taking into account excited states, and consideration of more and recently published one-particle approximations. Another recent paper [15] on our model system focuses its attention on the test of quantum-chemical methods and the singlet ground state for $\omega = \frac{1}{2}$. The two-electron system in external Coulomb potentials has been considered in [16].

This paper cannot provide an overall assessment of all currently used one-particle approximations for all kinds of systems. This task would take at least a review article, if not a book. Instead it focuses attention on a particular model, which contains many features of real systems, and the latest and some of the well established approximations

for excited states. In particular, we could not consider the approach using the DFT for ensembles [17] and the approach by Fritzsche [18].

2. Review of the exact solution

In this section we shall review the exact solution of the Schrödinger equation for our model [1]. We shall confine ourselves to those aspects which are helpful in understanding this paper. Its *Hamiltonian* reads

$$H = -\frac{1}{2}\nabla_1^2 + \frac{1}{2}\omega^2\mathbf{r}_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}\omega^2\mathbf{r}_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (1)$$

where \mathbf{r}_1 and \mathbf{r}_2 are the position operators of the two particles. (Atomic units $\hbar = m = e = 1$ are used throughout.) We now introduce the difference vector and the centre of mass as new variables:

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \quad (2)$$

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad (3)$$

in which the Hamiltonian decouples

$$H = -\nabla_r^2 + \frac{1}{4}\omega^2\mathbf{r}^2 + \frac{1}{r} - \frac{1}{4}\nabla_R^2 + \omega^2\mathbf{R}^2 \equiv H_r + H_R. \quad (4)$$

Since H is independent of spin, the total wavefunction can be factorized as follows

$$\psi(1, 2) = \varphi(\mathbf{r}) \cdot \xi(\mathbf{R}) \cdot \chi(s_1, s_2). \quad (5)$$

The *Pauli principle* demands that if χ is symmetric against particle exchange (triplet state) then φ must be antisymmetric $\varphi(-\mathbf{r}) = -\varphi(\mathbf{r})$ and if χ is antisymmetric (singlet state) then φ has to be symmetric $\varphi(-\mathbf{r}) = \varphi(\mathbf{r})$. In either case there is no constraint on $\xi(\mathbf{R})$ since \mathbf{R} is symmetric in itself. Thus the Pauli principle, which forces us to work with determinantal basis functions when treated in the coordinates \mathbf{r}_1 and \mathbf{r}_2 , is reduced to selecting solutions of definite parity and combining them with the appropriate spin part.

It follows from (4) that the *Schrödinger equation* $H\psi = E\psi$ separates into

$$\left[-\frac{1}{2}\nabla_r^2 + \frac{1}{2}\omega_r^2\mathbf{r}^2 + \frac{1}{2r} \right] \varphi(\mathbf{r}) = \varepsilon'\varphi(\mathbf{r}) \quad (6)$$

where $\omega_r = \frac{1}{2}\omega$ and $\varepsilon' = \frac{1}{2}\varepsilon$ and

$$[-\frac{1}{2}\nabla_R^2 + \frac{1}{2}\omega_R^2\mathbf{R}^2]\xi(\mathbf{R}) = \eta'\xi(\mathbf{R}) \quad (7)$$

where $\omega_R = 2\omega$ and $\eta' = 2\eta$. To establish a full analogy with well known problems, we defined new oscillator frequencies and energies for either problem and the total energy is $E = \varepsilon + \eta$. The normalization condition for ψ can be split into $\int d\mathbf{r} |\varphi(\mathbf{r})|^2 = 1$ and $\int d\mathbf{R} |\xi(\mathbf{R})|^2 = 1$.

Due to its importance in section 4, we wish to mention how the total angular momentum $\mathbf{L}_{\text{tot}} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2$ can be expressed in terms of the coordinates \mathbf{r} and \mathbf{R} . Straightforward analysis provides

$$\mathbf{L}_{\text{tot}} = \mathbf{r} \times \mathbf{p} + \mathbf{R} \times \mathbf{P} = \mathbf{l} + \mathbf{L}$$

where $\mathbf{p} = \frac{1}{i}\nabla_r$ and $\mathbf{P} = \frac{1}{i}\nabla_R$.

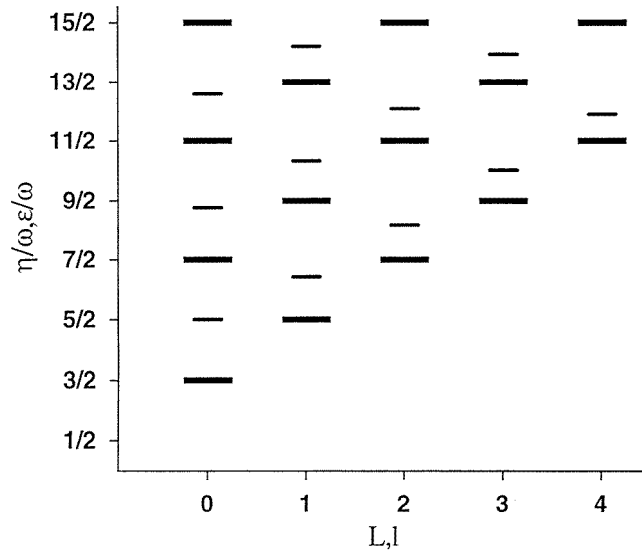


Figure 1. Term values of the 3D harmonic oscillator (7) according to $\eta_{NL}/\omega = (2N + L + \frac{3}{2})$ (wide and thick levels), where $N = 0, 1, 2, \dots$ and $L = 0, 1, 2, \dots$ are the node number and the angular momentum quantum number, respectively. Also given are the eigenvalues ε/ω of the Schrödinger equation in the relative coordinates (6) for $\omega = \frac{1}{2}$, which are shifted upwards owing to the Coulomb interaction (smaller levels).

The solution of the three-dimensional (3D) oscillator problem for the *centre-of-mass motion* (7) is well known and shall be repeated here for future reference. The eigenvalues are

$$\eta'_{NL} = \omega_R(2N + L + \frac{3}{2}) \quad (8)$$

where $N = 0, 1, 2, \dots$ and $L = 0, 1, 2, \dots$ are the node number and angular momentum quantum number, respectively. In order to make the discussion of excitation energies clearer, the term scheme of the 3D oscillator is included in figure 1. The radial part of the angular momentum representation of the eigenfunctions

$$\xi_{NLM}(\mathbf{R}) = \frac{U_{NL}(R)}{R} Y_{LM}(\hat{\mathbf{R}}) \quad (9)$$

can be found in textbooks on advanced quantum mechanics [25].

We now turn to the *relative motion* of both electrons. Here we introduce spherical coordinates which separate the modulus r from the angular coordinates $\hat{\mathbf{r}} = \mathbf{r}/r$, giving rise to the ansatz

$$\varphi(\mathbf{r}) = \frac{u(r)}{r} Y_{lm}(\hat{\mathbf{r}}) \quad (10)$$

where Y_{lm} are the spherical harmonics and $u(r)$ is determined by the radial Schrödinger equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{2} \omega_r^2 r^2 + \frac{1}{2r} + \frac{l(l+1)}{2} \frac{1}{r^2} \right] u(r) = \varepsilon' u(r). \quad (11)$$

Since $Y_{lm}(-\hat{\mathbf{r}}) = (-1)^l Y_{lm}(\hat{\mathbf{r}})$ we note that all eigensolutions satisfy the Pauli principle and that solutions corresponding to even (odd) l belong to the singlet (triplet) state.

Equation (11) can be solved numerically. It turns out, however, that for a discrete (but countably infinite) set of oscillator frequencies there are also analytical solutions [1]. These solutions have the form

$$u(r) = e^{-\frac{1}{2}\omega_r r^2} \cdot t(r) \quad (12)$$

with $t(r)$ being a polynomial $t(r) = r^{(l+1)} \sum_{v=0}^{(n-1)} A_v r^v$. The basic problem of how to find the set of solvable frequencies ω_r is described in more detail in [1]. Once they are found, the corresponding eigenvalues ε' follow from

$$\varepsilon' = \omega_r (n + l + \frac{1}{2}) \quad (13)$$

Thus the number n characterizes for a given angular momentum quantum number l and the number of nodes (or the degree of excitation) the solution in question. From (8) and (13) we obtain for the total energy in analytically solvable cases

$$E = 2\varepsilon' + \frac{\eta'}{2} = (n + l + 2N + L + 2)\omega = i\omega \quad (14)$$

Thus, the solvable ω_r are special, insofar as the total energy is an integer multiple of ω , as for noninteracting electrons. Moreover, since the highest occupied KS eigenvalue ε_F can be written as the difference between the total energy of the N_e and the $N_e - 1$ particle system, and the energy of the $N_e - 1 = 1$ particle system is a half-integer ($\frac{3}{2}, \frac{5}{2}, \dots$) multiple of ω , ε_F is a half-integer multiple of ω for solvable cases.

In addition to what has been published previously, we wish to draw attention to the fact that our model has an additional special feature. At least in the singlet and triplet ground state ($l = 0$ and 1 , respectively), the total wavefunction has *exactly* the form of a Jastrow ansatz, i.e. it is a product of a Slater determinant constructed from *bare* (or interaction free) oscillator eigenstates and a function of the relative coordinate $|\mathbf{r}_2 - \mathbf{r}_1|$. For the solvable set of ω_r this function is a known *finite* polynomial, for all other ω_r the polynomial has an infinite number of terms.

A further peculiarity concerns the oscillator model itself, not only the solvable ω_r . The singlet–triplet splitting is the same for all excited states. This feature and approximate calculations have been considered in [26]. More consequences from the special electron number $N_e = 2$ will be discussed in sections 3 and 4. The mention of all of these peculiarities should serve as a warning for the undue generalization of conclusions from this model.

Apart from numerically or analytically exact solutions of (1), in the following sections we will refer to an approximation in which the effective potential in (11)

$$V_{\text{eff}} = \frac{1}{2}\omega_r^2 r^2 + \frac{1}{2} \frac{1}{r} + \frac{l(l+1)}{2} \frac{1}{r^2} \quad (15)$$

is expanded around its minimum position r_{\min} in a Taylor series

$$V_{\text{eff}} = V_{\min} + \frac{1}{2}\omega_e^2 (r - r_{\min})^2 + \dots \quad (16)$$

and the resulting oscillator equation is solved analytically providing the eigenvalues

$$\varepsilon'_m = V_{\min} + \omega_e (m + \frac{1}{2}); \quad m = 0, 1, \dots \quad (17)$$

and the approximate ground-state wavefunction is

$$u_0(r) = \left(\frac{\omega_e}{\pi}\right)^{1/4} e^{-\frac{1}{2}\omega_e (r - r_{\min})^2}$$

with V_{\min} and ω_e depending on l . This approximation has already been used in dimensional scaling (see, for example, [19]) and it has been included in this paper in order to demonstrate how good it is for smaller ω_r . For helium it is applicable to $D \geq 5$ only, in our case to all dimensions D (for peculiarities in $D = 2$ connected with the fact that the centrifugal potential is negative for $l = 0$ see [20]).

3. Ground state

Before we present our numerical results, we wish to discuss the simplifications rendered possible by our special model.

In HF and in the singlet ground-state configuration we can express the exchange energy by means of the Hartree energy $E_x = -\frac{1}{2}E_H$ and so

$$E^{\text{HF}} = T + V + \frac{1}{2}E_H$$

where T and V are the kinetic energy and the interaction energy with the external potential, respectively, and E_x and E_H do contain the self-interaction terms in this notation. Therefore, this case can be treated numerically with a usual LSDA program where the XC correction is dropped and the Hartree energy is multiplied by a factor of $\frac{1}{2}$. This does not hold for the excited singlet state and for all triplet state configurations.

The total energy in the LSDA reads

$$E^{\text{LSDA}} = T + V + E_H + E_{xc}^{\text{LSDA}}$$

where $E_{xc}^{\text{LSDA}}[n_+, n_-] = \int d^3r n(\mathbf{r}) \varepsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r}))$, n is the total density and n_+ and n_- are the up and down spin densities. In LSDA + SIC we subtract the self-interaction terms ΔE_H and ΔE_{xc} in the following manner:

$$E^{\text{LSDA+SIC}} = T + V + E_H - \Delta E_H + E_{xc}^{\text{LSDA}} - \Delta E_{xc}^{\text{LSDA}}$$

where $\Delta E_H = \sum_i E_H[n_i]$ and $\Delta E_{xc}^{\text{LSDA}} = \sum_i E_{xc}^{\text{LSDA}}[n_i, 0]$. In singlet state configurations, we have $\Delta E_x^{\text{LSDA}} = E_x^{\text{LSDA}}$ and the self-interaction corrected LSDA exchange energy vanishes exactly, as it should, since there is no exchange between two electrons with different spin. Therefore, the exchange contribution is treated exactly here. This also holds for excited singlet configurations, but not for triplet states.

In figure 2 the results for the density of the singlet ground state for two solvable ω are shown. For the intermediate correlation regime $\omega = \frac{1}{2}$ (a), the LSDA result (we used the version by Perdew and Zunger [2]) is not localized enough, which coincides with what is known from atoms. The SIC-correction [2] to the LSDA changes the curve towards stronger localization, but overshoots considerably. The latest GGA [3] corrects in the wrong direction and produces a spurious charge accumulation in the asymptotic region. For this ω , HF provides the best density. It might be interesting to note that even in the strong correlation (small ω , low-density) limit shown in (b) the LSDA gives the correlation induced localization of the electrons *qualitatively* right, although the SIC correction is much better. Interestingly, the localization in the LSDA is too strong, unlike the behaviour discussed above. HF is not able to describe electron localization since it is driven by correlations, which are missing in HF. The self-consistent procedure including the GGA did not converge in this limit. In the weak correlation limit (large ω) the density is merely the sum of two Gaussians coming from two independent oscillator states (not shown).

The characteristic features of the density can be understood by means of the effective KS potential shown in figures 3(a) and (b). Amongst others, the exact KS potential is also given. The construction of the latter from the exact density is described in [10] and [12]. It must suffice here to mention that, by definition, the exact KS potential reproduces the exact density and that this result is available (at present, but not in principle) only for the singlet state.

In the intermediate correlation regime (figure 3(a)), the effective LSDA potential is too shallow (as already discussed in [12, 13]), but otherwise qualitatively right. Because the SIC and the HF potentials (which are both self-interaction free) do not show this defect,

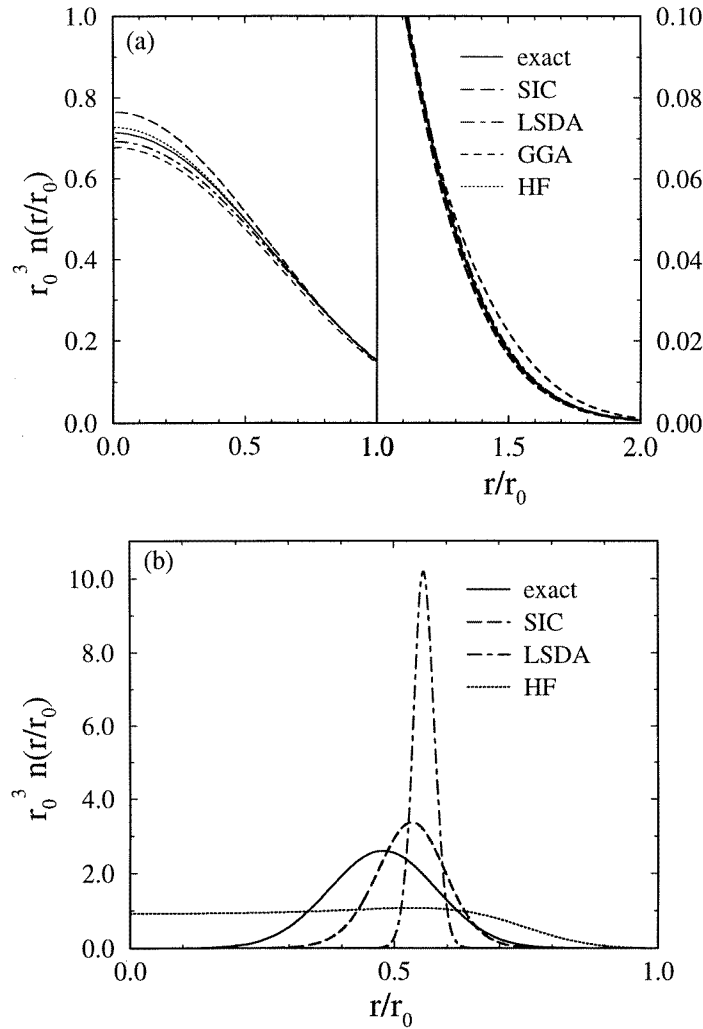


Figure 2. Comparison of the exact density of the singlet ground state of harmonium for (a) $\omega = \frac{1}{2}$ and (b) $\omega = 6.48771 \times 10^{-5}$ with different self-consistent one-particle approximations. The right-hand side of 2(a) is a blow-up of the asymptotic region. r_0 is the classical electron distance, which has been used for scaling purposes [1].

one could attribute this error to self-interaction. The GGA curve shows where the spurious charge accumulation comes from, namely the wiggle near $r = 1.5 r_0$. This wiggle was already present in former versions (see [12, 13]) and has obviously not been ‘weeded out’ completely in [3]. (Observe, however, that we are now using the self-consistent density instead of the exact one.) Figure 3(c) demonstrates that the location of the wiggle roughly coincides with the classical turning point $r_{cl} = \sqrt{3/\omega}$. It is obviously a relic of the semiclassical Kirzhnits expansion of the one-particle density matrix, which breaks down at r_{cl} and which forms the basis for the exchange part of the GGA considered here (see [3, 4] and references therein). It can also be considered as a consequence of the huge oscillations in the XC-hole derived from this approximation. The full curve in figure 3(c)

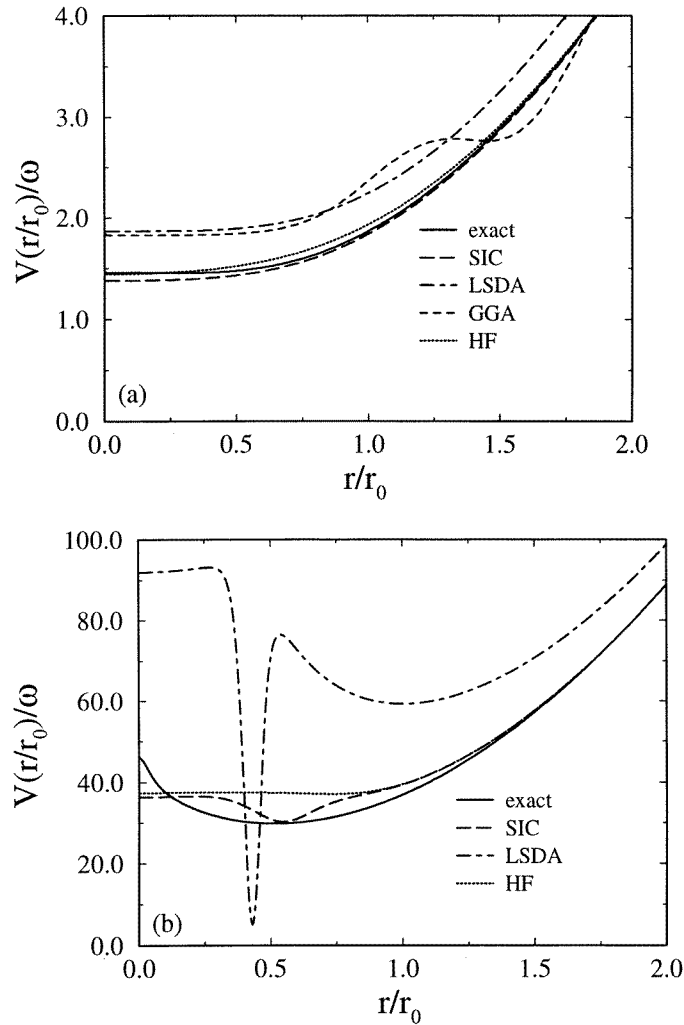


Figure 3. Comparison of the exact effective KS potential in the singlet state with some approximations for (a) $\omega = \frac{1}{2}$ and (b) $\omega = 6.48771 \times 10^{-5}$. r_0 is the classical electron distance, which is an appropriate scaling parameter in the strong correlation limit. (c) The sum of Hartree and XC potential for some larger ω within the GGA. The full curve is the exact result in the limit $\omega \rightarrow \infty$. r_{cl} denotes the classical turning point which is appropriate for scaling purposes in the weak correlation limit.

is the (rescaled) sum of the Hartree and the X potential in the limit $\omega \rightarrow \infty$, which reads

$$\frac{(v_H + v_x)}{\sqrt{\omega}} = \frac{\text{erf}(\sqrt{3}r/r_{cl})}{\sqrt{3}r/r_{cl}}.$$

This is simply the Hartree potential of a one-electron oscillator state. Observe that the correlation contribution can be neglected in this limit.

In the strong correlation regime (figure 3(b)), the exact KS potential exhibits a shallow minimum which gives rise to the localization of the electron near $r = 0.5r_0$. In the LSDA

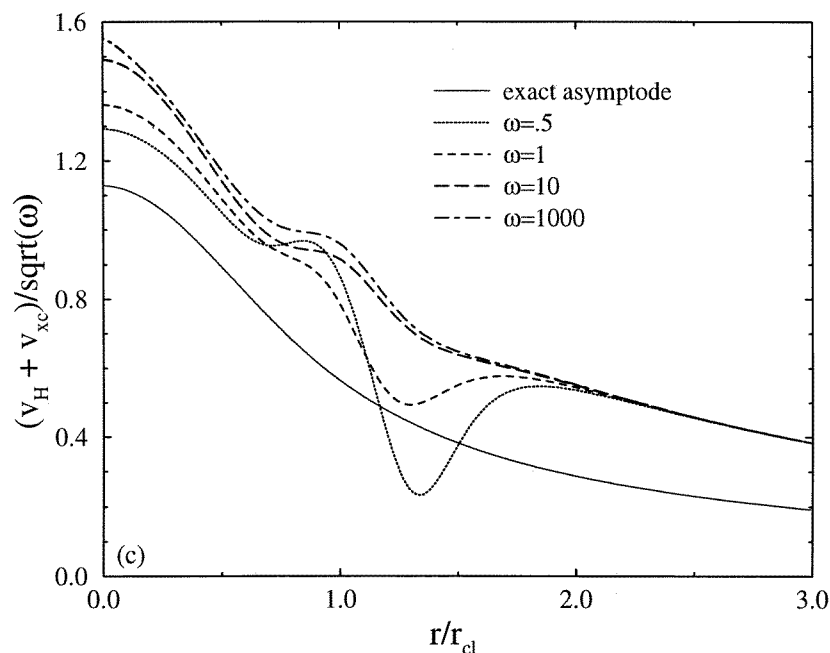


Figure 3. (Continued)

a sharp spike originating from the XC contribution appears. This spike also produces a localized density, but the corresponding peak in the density is much too narrow. One should also observe that the peak in the density is shifted towards larger r , compared with the position of the sharp minimum in the potential, owing to the influence of the second (relative) shallow minimum in the potential. The SIC-corrected potential is remarkably better although the dip at $r \approx 0.5r_0$ gives rise to a peak in the density which is also too narrow. The HF potential looks to be better than LSDA, but worse than SIC. However, it does not show a minimum so no localization in the density can be found. The most important conclusion from this figure is that the easiest way to correct the LSDA potential is to use a self-interaction free method. Clearly the influence of self-interaction decreases with the number of electrons and is usually less serious than in this case.

The ground-state energy of the singlet and triplet system is shown in figure 4 as a function of ω . It is amazing how well SIC does even in the strong-correlation (low-density) limit. This conclusion is in agreement with [10, 21], who studied the one-dimensional Hubbard model for a hydrogen chain. Therefore, a treatment of the Wigner crystal in LSDA + SIC seems to be reasonable. In agreement with experience gathered from atoms, the LSDA in the low-density limit is not as good for the energies as for the density. For $\omega = 10^{-5}$ the ground-state energy in the LSDA is strongly negative, although all of its contributions except for the XC contribution are positive definite. The exact result is also positive definite. Therefore, the negative total energy in the strong correlation limit is owing to an overestimation of the XC contribution (see also figure 3). For small ω , the approximation denoted by 'Taylor' is even better than LSDA + SIC. Unfortunately this precision cannot be maintained for excited states and this method cannot be applied to 3D external Coulomb potentials (see section 2). It is clear that by increasing the degrees of

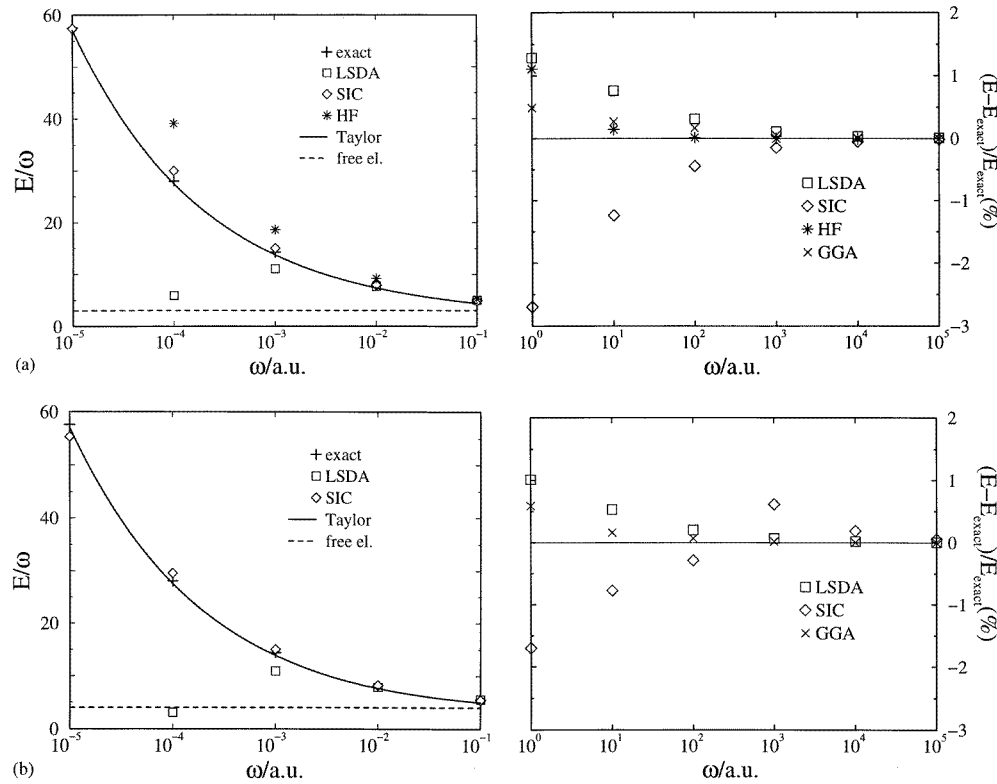


Figure 4. (a) Singlet and (b) triplet ground-state energy E/ω of harmonium as a function of ω for the approximations given in the inset. 'Taylor' means the result from (17), 'free electron' is the energy of two non-interacting electrons in the external oscillator potential. Observe, that in the right part ($\omega \geq 1$) the percentage error of the approximations is given instead of the total value. The E/ω values in the LSDA for $\omega = 10^{-5}$ are outside the range of the figure and are -40.42 and -79.10 for singlet and triplet, respectively. For HF in the singlet state the value at $\omega = 10^{-5}$ is 83.876 .

excitation, the wavefunction becomes less localized around the potential minimum and the error of the Taylor approximation around this minimum has increasing influence. For large ω , the effective potential curve around its minimum becomes more asymmetric and therefore the Taylor approximation is less precise without breaking down completely. Clearly, the one-particle approximations are superior over the Taylor approximation in the large ω limit. As expected, the ground-state energy in HF is too high, in particular for small ω . This is because in this limit correlations play the dominant role, which are missing in HF. It is amazing how precise the GGA ground-state energies are despite the poor charge densities. However, for small ω the self-consistent procedure for the GGA did not converge.

4. Excited states

If one sets out to compare excitation energies from completely different methods one has to deal with a huge bulk of data for each method. The main problem then is to find out which value from one method corresponds to which value from another method. Comparing

term schemes of one-particle energies (and not energy differences) would make this task easier, but this is not possible because in the exact solution one-particle energies are not well defined. So we have to select excitation energies due to certain principles out of the huge bulk of data, as for example, dipole-forbidden transitions from the ground state or any other state with a given total angular momentum. We stress that in all excitations considered in this paper the spin is conserved (no spin-flip processes).

Excitation energies within the one-particle approximations HF, LSDA, LSDA + SIC, and GGA have been calculated in the following three ways.

(i) Differences of self-consistent KS (or HF) one-particle eigenvalues in the effective ground-state potential

$$\Delta E_{if}^{\text{KS}} = \varepsilon_f^{\text{KS}} - \varepsilon_i^{\text{KS}}.$$

This approximation has been shown to be the zeroth approximation in a perturbation expansion with respect to the coupling constant [7]. (All excitation energies from one-particle approximations presented in the tables are eigenvalue differences, unless otherwise stated.)

(ii) Differences of self-consistent total energies calculated from the excited $\{n_k\}_f$ and the ground-state $\{n_k\}_i$ configurations

$$\Delta E_{if}^{\text{tot}} = E^{\text{tot}}(\{n_k\}_f) - E^{\text{tot}}(\{n_k\}_i). \quad (18)$$

Apart from special cases (where both configurations are ground states of different symmetry [8]) this approximation has no formal justification. We shall emphasize that $\Delta E_{if}^{\text{tot}}$ only consists of two terms. The modifications described in [22] are considered in [27].

(iii) Differences of self-consistent KS (or HF) eigenvalues within the STS configuration

$$\Delta E_{if}^{\text{STS}} = \varepsilon_f^{\text{STS}} - \varepsilon_i^{\text{STS}}$$

i.e. $\varepsilon_{f,i}^{\text{STS}}$ are self-consistent eigenvalues of the KS (or HF) equation where the initial and final one-particle state are half-occupied; the other states are occupied as in the ground state. Using Janak's theorem, this approximation can be shown to agree with (ii) in first order in the difference of the final- and initial-state occupation (see, for example, section 4.4 of [23]).

'LSDA + SIC' needs some special explanation. If used for the one-particle energy differences in (i) the initial (ground) state ε_i is calculated from an effective potential which includes the usual SIC correction, whereas the effective potential used for the final (excited) state ε_f is in the usual LSDA. However, both effective potentials are calculated from the same (ground-state) density which includes the SIC. On the other hand, for the total energy differences (ii) the SIC correction is included in both total energies. In order to maintain the connection between total energy differences and the STS concept mentioned above, we also included the SIC in STS for the half-occupied excited state, i.e. we subtracted $v_{\text{H}}[|\varphi_f(r)|^2/2] + v_{\text{xc}}[|\varphi_f(r)|^2/2]$ from that LSDA potential which provides the excited-state energy ε_f .

The correction formula by PGG [6] to the LSDA excitation energies (denoted by 'LSDA + PGG' in the tables) reads

$$\Delta E_{if} = \Delta E_{if}^{\text{KS}} + 2 \text{Re} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_f(\mathbf{r}_2) \times \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} + f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2, \Delta E_{if}^{\text{KS}}) \right] \phi_f^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2)$$

where $\phi_i(\mathbf{r})$ and $\phi_f(\mathbf{r})$ are the initial and final KS one-particle states in the LSDA and the local version for the kernel f_{xc} given in [6] has been used. Thus our results for this treatment are consistently in a local approximation.

Görling [7] derived a formula in first-order perturbation theory in the coupling constant. If the exact KS orbitals and eigenvalues are used, it simplifies to:

$$\Delta E_{if} = \Delta E_{if}^{\text{KS-exact}} + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_f(\mathbf{r}_2) \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \phi_f^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2).$$

These results are denoted by ‘KS-exact + G’. In both correction formulae only singlet transitions are considered here. Spin-flip processes will be discussed in a separate paper.

4.1. Dipole-allowed optical transitions

In the exact solution, there are optical dipole excitations in the centre-of-mass subspace only, since the optical transition operator $(\mathbf{r}_1 + \mathbf{r}_2)$ may be expressed merely by means of the centre of mass coordinate \mathbf{R} and therefore the transition probability is zero for all transitions involving excitations in the relative coordinate subspace.

$$\langle \chi_{LM}(\mathbf{R}) \phi_{lm}(\mathbf{r}) | (\mathbf{r}_1 + \mathbf{r}_2) | \chi_{L'M'}(\mathbf{R}) \phi_{l'm'}(\mathbf{r}) \rangle = \langle \chi_{LM}(\mathbf{R}) | 2\mathbf{R} | \chi_{L'M'}(\mathbf{R}) \rangle \langle \phi_{lm}(\mathbf{r}) | \phi_{l'm'}(\mathbf{r}) \rangle.$$

Thus, the selection rules read:

$$\Delta L = \pm 1 \quad \Delta M = 0, \pm 1 \quad \Delta l = 0, \quad \Delta m = 0$$

where the angular momentum quantum numbers L, M refer to the centre of mass coordinate subspace and l, m refer to the relative coordinate subspace. As the Schrödinger equation (7) for $\xi(\mathbf{R})$ is the same as for *one* particle in the oscillator potential, the exact optical excitation energies (in units of ω) comprise all odd numbers: $\Delta E/\omega = 1, 3, 5, \dots$ (see also figure 1). This holds for allowed transitions starting from any state. Therefore, allowed excitation energies in the exact treatment are not influenced by the electron–electron interaction and its influence in the DFT treatment must cancel. Thus this test is in a sense similar to the limiting case of one particle, where the Hartree and XC contributions must cancel. This type of correlation-independent excitation energy exists for any particle number in the external oscillator potential (or for free electrons in a homogeneous magnetic field [24]), because the centre-of-mass motion can always be separated. In one-particle approximations all one-particle excitations with $\Delta l_1 = \pm 1$, $\Delta m_1 = 0, \pm 1$ are dipole allowed, where (l_1, m_1) are now the angular momentum quantum numbers of the one-particle states.

In table 1 we show the lowest dipole-allowed excitation energies starting from the *singlet* ground state (having total angular momentum 0) for three correlation regimes (weak, intermediate and strong). In the exact treatment these are centre of mass excitations from $L = 0$ to $L = 1$. The relative coordinate subspace stays in its ground state with $l = 0$. This corresponds in the one-particle approximations to transitions from $l_1 = 0$ to $l_1 = 1$. For the strong and intermediate correlation regime an ω from the exactly solvable set had to be chosen in order to be able to include the exact KS potential into the considerations. The latter is available to us only for these exactly solvable cases. In the low-correlation limit no exactly solvable ω exist. However, this limit is not very interesting since the electrons behave virtually like noninteracting ones. Investigation of table 1 leads to the following conclusions.

In the *strong correlation limit*, table 1(a), the LSDA results for the excitation energies are catastrophic. This strange spectrum is a consequence of the peculiarities of the effective

Table 1. Dipole-allowed optical excitation energies (in units ω) for *singlet* transitions starting from the ground state with total orbital angular momentum $L_{\text{tot}} = 0$. All data are given for the following three correlation regimes:

(a) strong correlation with $\omega = 6.48771 \times 10^{-5}$

(b) intermediate correlation with $\omega = \frac{1}{2}$ and

(c) weak correlation $\omega = 10^5$.

Unless otherwise stated, the excitation energies from one-particle approximations are differences of KS or HF eigenvalues. The abbreviations for the methods are explained in the text. In the intermediate correlation regime figure 1(b) and for the three lowest excitations, the excitation energies are also calculated as differences of total energies and from the concept of STS. The latter results are the second and third values in each cell of the table. A rule indicates that no convergency could be reached. The numbers in parentheses (where given) are the error of the approximate results compared with the exact one, given as a percentage.

(a)

Exact	HF	KS-exact	LSDA	LSDA + SIC
1	0.088	0.104	0.137	-3.410
3	0.687	1.443	34.026	5.063
5	1.418	2.800	34.690	12.473
7	2.313	4.179	36.427	18.754
9	3.337	5.586	38.167	23.758

(b)

Exact	HF	KS-exact	KS-exact + G	LSDA	LSDA + PGG	LSDA + SIC	GGA
	From ϵ^{HF}	From ϵ^{KS}	From ϵ^{KS}	From ϵ^{KS} From E^{tot} From ϵ^{STS}	From ϵ^{KS}	From ϵ^{KS} From E^{tot} From ϵ^{STS}	From ϵ^{KS} From E^{tot} From ϵ^{STS}
1	0.841(-15.9)	0.843(-15.7)	1.024(+2.4)	0.832(-16.8) 0.831(-17.0) 0.831(-16.9)	1.063(+6.3)	1.307(+30.7) 0.863(-13.7) 0.858(-14.2)	0.784(-21.6) 0.824(-17.6) 0.818(-18.2)
3	2.721(-9.3)	2.742(-8.6)	2.808(-6.4)	2.737(-8.8) 2.703(-9.9) 2.701(-9.9)	2.812(-6.3)	3.210(+7.0) 2.768(-7.7) 2.758(-8.1)	2.543(-15.2) — —
5	4.644(-7.1)	4.673(-6.5)	4.710(-5.8)	4.664(-6.7) 4.623(-7.5) 4.620(-7.6)	4.701(-6.0)	5.135(+2.7) 4.702(-6.0) 4.690(-6.2)	4.619(-7.6) — —
7	6.589(-5.9)	6.623(-5.4)	6.648(-5.0)	6.604(-5.7)	6.625(-5.4)	7.073(+1.1)	6.556(-6.4)
9	8.547(-5.0)	8.584(-4.6)	8.603(-4.4)	8.553(-5.0)	8.565(-4.8)	9.022(+0.2)	8.512(-5.4)

(c)

Exact	HF	LSDA	LSDA + SIC
1	0.999 59	0.999 52	1.000 90
3	2.999 25	2.999 21	3.000 59
5	4.999 10	4.998 99	5.000 37
7	6.998 96	6.998 82	7.000 20
9	8.998 85	8.998 68	9.000 06

potential (see figure 3(b)) with a narrow and a wide minimum. The overall behaviour of the SIC spectrum is much more civilized, although it shows the defect that the state which should be the first excited state is lower in energy than the ground-state energy (therefore this excitation energy is negative). The reason for this is that the first excited state is the lowest eigenvalue in an LSDA-like potential for $l_1 = 1$ (calculated from the SIC density) which shows a spike similar to that shown in figure 3(b). This gives a lower eigenvalue (although the positive definite centrifugal potential has to be added) than the ground state in the SIC potential. In other words, the SIC potential is not lower than the LSDA potential in all cases. Unlike in atomic and solid-state physics, the LSDA provides, in most cases, excessively large excitation energies in this limit (with the exception of the lowest excitation). The reason for this is that the lowest two one-particle states are trapped in the spike of the potential. The best results come from the exact KS potential. From figure 3 it is clear that this parabola-like potential is the only one which can nearly reproduce the equidistant spectrum found in the exact treatment. The HF method is close to the exact KS result, but is somewhat worse. The GGA is not included in this table since the self-consistent treatment did not converge and the results by PGG are not shown because this method is meant for small corrections and cannot correct the large LSDA error. The correction by PGG (which is not shown in figure 1(a)) moves in the right direction, but is quantitatively wrong. The first LSDA excitation energy (0.137), which is unexpectedly reasonable, is shifted to 4.286, and the higher excitation energies, which are much too large in the LSDA, are shifted downwards, but are much too small.

In the *intermediate correlation regime*, table 1(b), LSDA, HF, and the exact KS potential are virtually equivalent. The correction by PGG [6] (denoted by 'LSDA + PGG') always increases the excitation energy with respect to the LSDA, but the error of the lowest excitation energy is overcompensated and for the higher excitations the correction is systematically too small. The first-order correction by Görling [7] (denoted by 'KS-exact + G') shows virtually the same features. The GGA gives no improvement of the excitation energies as compared with the LSDA.

For the intermediate correlation regime we also compared the results from the difference of KS energies with the differences of total energies and with the difference of KS energies in the STS. The conclusion is that the STS result represents the total energy difference very well in all cases. The difference of KS energies, on the other hand, is also a good representation of the total energy difference, except if the SIC is included. Thus, for SIC calculations one should calculate excitation energies from total energy differences or the STS concept. Trials to calculate excitation energies from GGA total energy differences failed because the self-consistent procedure did not converge for the state with the excited configuration. This could be concerned with the wiggle in the effective potential (see above).

In the *weak-correlation regime*, table 1(c), the LSDA again generates too small excitation energies and the LSDA + SIC changes from being too large to too small with increasing excitations. (The higher excitations, where the excitation energy in LSDA + SIC is too small, are not shown in table 1(c). The tendency is obvious, though.) The best results are provided by HF, since it treats exchange exactly and the missing correlations are of minor importance in this limit. The correction to the LSDA by PGG (not shown in table 1(c)) is too small by at least four orders of magnitude for all excitations. Thus, all in all, the correction of the lowest excitation energy by PGG changed from too large (for strong correlations) to too small (for weak correlations). Clearly there is an ω in between where it is just right. This ω might

Table 2. Dipole-allowed optical excitation energies (in units ω) for *triplet* transitions starting from the ground state with total orbital angular momentum $L_{\text{tot}} = 1$. The three numbers in each cell correspond to a spurious splitting in one-particle treatments (see text). Data are given for the three correlation regimes adopted in figure 1.

(a)			(b)		
Exact	LSDA	LSDA + SIC	Exact	LSDA	LSDA + SIC
1	34.373 0.294 forbidden	5.010 −3.738 forbidden	1	0.991(−0.9) 0.921(−7.9) forbidden	1.344(+34.4) 1.272(+27.3) forbidden
3	34.954 34.450 34.532	12.837 5.276 5.190	3	2.925(−2.5) 2.888(−3.7) 2.815(−6.2)	3.276(+9.2) 3.237(+7.9) 3.307(+10.2)
5	36.109 35.390 35.253	19.411 13.107 13.016	5	4.871(−2.6) 4.848(−3.0) 4.765(−4.7)	5.221(+4.4) 5.196(+3.9) 5.255(+5.1)
7	37.850 36.187 36.269	24.556 19.681 19.589	7	6.826(−2.5) 6.808(−2.7) 6.713(−4.1)	7.174(+2.5) 7.156(+2.2) 7.208(+3.0)
9	39.594 37.928 38.009	27.556 24.808 24.729	9	8.786(−2.4) 8.773(−2.5) 8.678(−3.6)	9.134(+1.5) 9.119(+1.3) 9.167(+1.8)
(c)					
Exact	LSDA	LSDA + SIC			
1	0.999 93 0.999 79 forbidden	1.000 94 1.000 80 forbidden			
3	2.999 78 2.999 69 2.999 47	3.000 79 3.000 70 3.000 85			
5	4.999 64 4.999 57 4.999 36	5.000 64 5.000 58 5.000 74			
7	6.999 52 6.999 47 6.999 23	7.000 53 7.000 48 7.000 61			
9	8.999 41 8.999 37 8.999 11	9.000 42 9.000 38 9.000 49			

describe the regime where this method has been tested before [6]. For higher excitation energies the correction is always too small. In PGG everything depends on the quality of the *local* XC correction kernel $f_{xc}(\omega, n(\mathbf{r}))$. Its frequency dependence has been interpolated between $\omega = 0$ and ∞ . In between it is therefore rather uncertain. In principle one could use the harmonium spectrum to determine this ω dependence more exactly.

Table 3. Dipole-forbidden optical excitation energies (in units ω) for transitions between *singlet* states for fixed total orbital angular momentum $L_{\text{tot}} = 0$. Data are given for $\omega = \frac{1}{2}$ using the same methods as in table 1. The percentage errors in parentheses refer to the exact excitations in the R subspace.

Exact	HF	KS-exact	KS-exact + G	LSDA	LSDA + PGG	LSDA + SIC	GGA
R -excit. [r -excit.]	From ϵ^{HF}	From ϵ^{KS}	From ϵ^{KS}	From ϵ^{KS} From E^{tot} From ϵ^{STS}	From ϵ^{KS}	From ϵ^{KS} From E^{tot} from ϵ^{STS}	From ϵ^{KS}
2 [1.880]	1.799(−10.1)	1.823(−8.8)	1.956(−2.2)	1.818(−9.1) 1.778(−11.1) 1.779(−11.1)	1.996(−0.2)	2.295(+14.8) 1.840(−8.0) 1.836(−8.2)	1.617(−19.1) — —
4 [3.801]	3.694(−7.7) 3.731(−6.7) 3.731(−6.7)	3.724(−6.9)	3.781(−5.5)	3.719(−7.0) 3.665(−8.4) 3.662(−8.4)	3.783(−5.4)	4.192(+4.8) 3.748(−6.3) 3.740(−6.5)	3.662(−8.5) — —
6 [5.744]	5.625(−6.3)	5.660(−5.7)	5.693(−5.1)	5.645(−5.9) — 5.591(−6.8)	5.678(−5.4)	6.117(+2.0) 5.687(−5.4) 5.677(−5.4)	5.576(−7.1) — —
8 [7.699]	7.574(−5.3)	7.612(−4.9)	7.635(−4.6)	7.587(−5.2)	7.605(−4.9)	8.056(+0.7)	7.549(−5.6)
10 [9.663]	9.536(−4.6)	9.575(−4.2)	9.592(−4.1)	9.538(−4.6)	9.548(−4.5)	10.007(+0.1)	9.505(−5.0)

Table 2 contains the same information as table 1 except for the fact that we consider dipole allowed transitions starting from the *triplet* ground state (having a total orbital angular momentum 1) to other triplet states. In the one-particle picture there are three possibilities. The excitation can start from the $l_1 = 1$ ground state to final states with $l_1 = 0$ (upper values in each cell of table 1) and $l_1 = 2$ (middle values), or from the $l_1 = 0$ ground state to $l_1 = 1$ (lower values). (The lowest excitation from $l_1 = 0$ to $l_1 = 1$ is forbidden by the Pauli principle.) All three excitations are degenerate for noninteracting electrons and in the exact treatment, but not in the one-particle approximations. In the exact treatment there is only one possibility, i.e. centre-of-mass excitations from $L = 0$ to $L = 1$, whereby the relative coordinate subspace stays in its ground state with $l = 0$. Thus the amount of this spurious splitting is already an indication for the errors in the one-particle treatments. As mentioned earlier, HF and exact KS results for the triplet states are not available to us and LSDA + PGG and GGA have not been done. For the LSDA with and without SIC we find the following. In the strong correlation limit, both the LSDA and LSDA + SIC generate excessively large excitation energies (except for the first excitation) and SIC is remarkably better (with one exception which should be considered as accidentally). This general conclusion agrees with the singlet state. In the intermediate and weak correlation regime, LSDA and LSDA + SIC excitation energies are too small and too large, respectively, also in qualitative agreement with the singlet state.

4.2. Dipole-forbidden transitions

In this case we chose to investigate transitions among states with fixed angular momentum $L_{\text{tot}} = 0$ and 1, for singlet and triplet states, respectively. Unfortunately, the

number of possibilities which satisfy this condition is still so large that the one-to-one correspondence between exact and one-particle excitations is not obvious. In order to find out which exact excitation belongs to which one-particle excitation, we consider only those possibilities which give for vanishing electron–electron interaction the same excitation energy ΔE^0 .

Consider, for example, the lowest singlet excitation with $\Delta E^0/\omega = 2$. In the exact treatment there are two possibilities. There is a pure centre-of-mass excitation (***R***-excitation) with $L = 0$ and $N = 0 \rightarrow 1$ and a pure relative coordinate excitation (***r***-excitation) with $l = 0$ and $n = 0 \rightarrow 1$. The corresponding exact excitation energies $\Delta E/\omega$ are 2 and 1.8802 (for $\omega = \frac{1}{2}$). Both excitations are dipole forbidden and fulfil the above criteria. In the one-particle picture we have a one-particle excitation with $l_1 = 0$ and $n_1 = 0 \rightarrow 1$ and a two-particle excitation, where both electrons jump from the ground state to $l_1 = 1$ and $n_1 = 0$. The corresponding total energy differences within the LSDA are 1.7773 and 1.7146. In order to keep $L_{\text{tot}} = 0$, the orbital angular momenta of both electrons must be antiparallel.

For the next higher excitation with $\Delta E^0/\omega = 4$ there are four possibilities in the exact treatment: the pure ***R***-excitation, the pure ***r***-excitation, and two excitations where both the ***R*** and the ***r*** space are excited. Again the pure ***R***-excitation provides the largest excitation energy $\Delta E/\omega = 4$. The pure ***r***-excitation is the third largest with $\Delta E/\omega = 3.8011$. In the one-particle picture there are also four possibilities where the pure one-particle excitation with $l_1 = 0$ and $n_1 = 0 \rightarrow 2$ provides the largest excitation energy of $\Delta E/\omega = 3.6634$.

For all *singlet* excitations, which keep $L_{\text{tot}} = 0$ fixed, we observe the following. The largest excitation energy in the exact treatment is provided by pure ***R***-excitations between $L = 0$ states, in the one-particle treatment by pure one-particle excitations between $l_1 = 0$ states. Therefore, from the order of energies, it is justified to assign these two series to each other. Since the pure ***r***-excitations are also considered to be basic, we have included them in tables 3 and 4 as well (in brackets). They shall *not* be directly compared with the results from one-particle approximations. All combined (i.e. centre-of-mass *and* relative

Table 4. Dipole-forbidden optical excitation energies (in units ω) for transitions between *triplet* states for fixed total orbital angular momentum $L_{\text{tot}} = 1$. The oscillator frequency is $\omega = \frac{1}{2}$. The percentage errors in parentheses refer to the exact excitations in the ***R*** subspace.

Exact	LSDA	LSDA + SIC
<i>R</i> -excit.		
[<i>r</i> -excit.]		
2	1.937(−3.1)	2.288(+14.4)
[1.938]		
4	3.887(−2.8)	4.236(+5.9)
[3.893]		
6	5.841(−2.7)	6.189(+3.2)
[5.859]		
8	7.800(−2.5)	8.148(+1.8)
[7.831]		
10	9.764(−2.5)	10.111(+1.1)
[9.808]		

coordinate) excitations are omitted.

For *triplet* excitations, in the exact treatment also the pure *R*-excitations with $L = 0$ give the largest energies. Applying the same principle as above, these values should be compared with one-particle excitations of the $l_1 = 1$ state, where the $l_1 = 0$ electron remains in the ground state. The latter provide the largest excitation energies in the one-particle approximation. We wish to emphasize, however, that in the case of dipole-forbidden transitions the correspondence between excitations in the one-particle and the exact treatment is not beyond any doubt. The total spin and orbital angular momentum do not restrict the bulk of possibilities in such a way that a unique one-to-one correspondence can be established. Therefore the conclusions from this section should be treated with a degree of caution.

Table 3 is the counterpart of table 1(b), but for dipole-forbidden singlet transitions instead of allowed ones. Except for the fact that the corrections by Görling and PGG do not overcompensate the error of the KS excitation energies in this case, all conclusions agree qualitatively with figure 1(b). Tables 4 and 2(b) (forbidden and allowed triplet transitions) also give virtually the same information. This provides some evidence that our interpretation of the forbidden exact transitions in terms of one-particle transitions is correct.

5. Summary

We now summarize the most important conclusions in a qualitative way (for figures see above). We shall order the information by methods and not by measurable quantities, as done in the preceding sections. *All statements refer to the intermediate correlation case $\omega = \frac{1}{2}$, unless otherwise stated. It is understood without additional mention that all statements apply (strictly speaking) to the potential family considered here.* In particular LSDA + SIC requires special care if applied to other systems such as molecules and solids. These problems are connected to the fact that LSDA + SIC is not invariant under unitary transformation of the eigenstates. Furthermore, the two-electron *singlet* system is special insofar as LSDA + SIC provides the exact (namely vanishing) exchange energy. However, this does not hold for *triplet* states.

- The LSDA as the most common one-particle approximation gives amazingly good electron densities. Even in the strong correlation limit the densities are qualitatively right. The KS potential is systematically too shallow owing to self-interaction. Excitation energies are very close to those from the exact KS potential so that nonlocal corrections can hardly do any better. The ground-state energy, on the other hand, is remarkably improved by the (nonlocal) GGA.

- LSDA + SIC is very precise for ground-state energies in the strong correlation limit. Excitation energies should be calculated only from total energy differences in this method, since one-particle energy differences give poor results for excitation energies. For all other methods, using total energy differences or the Slater transition state is not much more precise than using KS energy differences (in LSDA it is even slightly worse).

- The latest GGA [3] provides the best ground-state energies (in the ‘chemical regime’), but the KS potential exhibits for all ω a wiggle near the classical turning point. Consequently the electron density shows a spurious charge accumulation in this region. This fact suggests the following procedure. Take LSDA densities (and not self-consistent GGA densities) for the calculation of total energies from the GGA energy functional. This also circumvents the (numerical) problems in the self-consistent procedure if the GGA XC potential is used. Excitation energies are not improved.

- The correction formula for LSDA excitation energies by PGG [6] provides shifts in the right direction. For dipole-allowed transitions, where the situation is clear, it overestimates and underestimates the correction for small and large excitation energies, respectively. The perturbation treatment by Görling [7] shows in first order virtually the same features.

- HF, which is identical to OEP for two particles in the singlet ground state, is superior to the LSDA for the KS potential, but for densities and excitation energies it is virtually equivalent. In the strong correlation regime, however, HF has serious problems.

Acknowledgments

We thank Professor E K U Gross, Professor J Perdew and Dr Görling for helpful discussions and the Deutsche Forschungsgemeinschaft for financial support.

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