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ARTICLE *in* JOURNAL- CHINESE CHEMICAL SOCIETY TAIPEI · JUNE 1999

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Recent New Developments of Steady-State and Time-Dependent Density Functional Theories for the Treatment of Structure and Dynamics of Many-Electron Atomic, Molecular, and Quantum Dot Systems

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We present a short account of recent new developments of density-functional theory (DFT) for accurate and efficient treatments of the electronic structure and quantum dynamics of many-electron systems. The conventional DFT calculations contain spurious self-interaction energy and improper long-range potential, preventing reliable description of the excited and resonance states. We present a new DFT with optimized effective potential (OEP) and self-interaction-correction (SIC) to overcome some of the major difficulties encountered in conventional DFT treatments using explicit energy functionals. The OEP-SIC formalism uses only orbital-independent single-particle local potentials and is self-interaction free, providing a theoretical framework for accurate description of the excited-state properties and quantum dynamics. Several applications of the new procedure are presented, including: (a) the first successful DFT treatment of the atomic autoionizing resonances, (b) a relativistic extension of the OEP-SIC formalism for the calculation of the atomic structure with results in good agreement with the experimental data across the periodic table ($Z=2-106$), (c) electronic structure calculation of the ionization properties of molecules, and (d) the delicate "shell-filling" electronic structure in quantum dots. Finally we present also new formulations of time-dependent DFT for nonperturbative treatment of atomic and molecular multiphoton and nonlinear optical processes in intense and superintense laser fields. Both the time-independent Floquet approach and the time-dependent OEP-SIC technique are introduced. Application of the time-dependent DFT/OEP-SIC procedure to the study of multiple high-order harmonic generation processes in intense ultrashort pulsed laser fields is discussed in detail.

INTRODUCTION

In recent years, the density-functional theory (DFT) has become a widely used formalism for electron structure calculations of atoms, molecules, and solids.¹⁻⁵ The DFT is based on the earlier fundamental work of Hohenberg and Kohn⁶ and Kohn and Sham.⁷ In the Kohn-Sham DFT formalism,⁷ the electron density is decomposed into a set of orbitals, leading to a set of one-electron Schrödinger-like equations to be solved self-consistently. The Kohn-Sham equations are structurally similar to the Hartree-Fock equations but include in principle exactly the many-body effects through a local exchange-correlation (xc) potential. Thus DFT is computationally much less expensive than the traditional *ab initio* many-electron wavefunction approaches and this accounts for its great success for large systems. However, the DFT is well developed mainly for the ground-state properties only. The treatment of excited states and

time-dependent processes within the DFT is much less developed.

The essential element of DFT is the input of the xc energy functional whose exact form is unknown. The simplest approximation for the xc-energy functional is through the local spin-density approximation (LSDA)^{1,8} of homogeneous electronic gas. A severe deficiency of the LSDA is that the xc potential decays exponentially and does not have the correct long-range behavior. As a result, the LSDA electrons are too weakly bound and for negative ions even unbound. More accurate forms of the xc-energy functionals are available from the generalized gradient approximation (GGA),⁹⁻¹² which takes into account the gradient of electron density. However, the xc potentials derived from these GGA energy functionals suffer similar problems as in LSDA and do not have the proper long-range Coulombic tail $-1/r$ either. Thus while the total energies of the ground states of atoms and molecules predicted by these GGA den-

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sity functionals⁹⁻¹² are reasonably accurate, the excited-state energies and the ionization potentials obtained from the highest occupied orbital energies of atoms and molecules are far from satisfactory, typically 40 to 50% too low.¹³ The problem of the incorrect long-range behavior of the LSDA and GGA energy functionals can be attributed to the existence of the self-interaction energy.^{13,14} For proper treatment of atomic and molecular dynamics such as collisions or multiphoton ionization processes etc., it is necessary that both the ionization potential and the excited-state properties be described more accurately. This article addresses new methods for overcoming some of the difficulties encountered by the conventional DFT.

In the following, we briefly describe some new developments in DFT recently carried out at the University of Kansas for accurate and efficient treatment of both ground- and excited-state properties of atomic, molecular, and quantum dots systems. Also presented are several new developments in time-dependent DFT for nonperturbative treatment of multiphoton dynamics and nonlinear optical processes of atoms and molecules in intense and superintense laser fields.

DFT WITH OPTIMIZED EFFECTIVE POTENTIAL AND SELF-INTERACTION CORRECTION: NEW APPROACH FOR IMPROVING CONVENTIONAL STEADY-STATE DFT

In the Kohn-Sham (KS) DFT formulation,⁷ one solves the following set of one-electron Schrödinger-like equation for N -electron systems (in atomic units),

(1)

where $v_{\text{eff},\sigma}(\mathbf{r})$ is the effective KS potential and σ is the spin index. The total density is given by

(2)

and the ground-state wavefunction is determined by

(3)

The total energy of the ground state is obtained by the

minimization of the Hohenberg-Kohn energy functional^{1,6}

(4)

Here T_s is the non-interacting KS kinetic energy,

(5)

$v_{\text{ext}}(\mathbf{r})$ is the "external" potential due to the electron-nucleus interaction, $J[\rho]$ is the classical electron-electron repulsive energy,

(6)

and $E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}]$ is the exchange-correlation energy. Minimization of the total energy functional Eq. (4) subject to the constraint

(7)

gives rise to the KS equations (1) with the effective potential

(8)

where $v_{\text{xc},\sigma}(\mathbf{r})$ is the exchange-correlation (xc) potential,

(9)

The KS equations are to be solved self consistently, starting from some initial estimate of the density $\rho_{\sigma}(\mathbf{r})$, until, convergence is reached. In actual calculations, the KS Hamiltonian in Eq. (1) must be fixed by a particular choice of the xc energy functional, $E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}]$. However, both LSDA and GGA energy functional forms contain spurious self-interaction contributions. Such self-interaction contribution can be seen from Eq. (4), where the last two terms $J[\rho]$ and $E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}]$ should in principle cancel each other exactly in the limit of a one-electron system, if the exact form for $E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}]$ is used. In practice, $E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}]$ needs to be approximated, leading to the self-interaction energy. The

existence of such self-interaction energy is the main source of error responsible for the incorrect long-range behavior of the exchange-correlation potential $v_{xc,\sigma}(\mathbf{r})$. Thus the elimination of the self-interaction contribution is essential for the proper treatment of the ionization potentials and excited-state properties.

Our approach for improving $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$ is based on the generalization of the so-called optimized effective potential (OEP) formalism.^{15,16} In this approach, one solves a set of one-electron equations, similar to the KS equations in Eq. (1),

$$(10)$$

The optimized effective potential, $V_{\sigma}^{OEP}(\mathbf{r})$, is obtained by the requirement that the spin-orbitals $\{\phi_{i\sigma}\}$ in Eq. (10) are those that minimize the total energy functional $E[\{\phi_{i\uparrow}, \phi_{j\downarrow}\}]$

$$(11)$$

where

$$(12)$$

Eq. (11) can be written as, using the chain rule for functional derivative,

$$(13)$$

While the physical idea of the OEP method is simple and appealing, Eq. (13) leads to an integral equation which is computationally impractical to solve. Recently, Krieger, Li, and Iafrate (KLI)¹⁷ have worked out an approximate, albeit accurate, procedure to circumvent this difficulty, reducing the determination of V_{σ}^{OEP} to the solution of simple linear equations. In all the KLI calculations so far,¹⁷ however, the exchange part of the density functional contains Hartree-Fock-like nonlocal potential. While such a procedure provides accurate results for the exchange part of E_{xc} , it is computationally more expensive than the traditional DFT calculations where only local single-particle potentials are

used. Thus we are interested in exploring an approximate and yet accurate procedure within the KLI framework involving only the use of local potentials. This would greatly speed up the computations of the static and dynamical properties of many-electron systems. Such a simplified procedure is particularly desirable when the time-dependent processes are considered. In the latter case, one needs to reconstruct the optimized effective potential for each small time step. As will be shown below, the proposed self-interaction-correction (SIC) procedure, similar to the original KLI method, allows also the construction of a self-interaction-free effective potential that is orbital independent. Further, the optimized effective potential so constructed, denoted by $V_{KLI,\sigma}^{SIC}(\mathbf{r})$ below, has the proper long-range ($-1/r$) behavior and thus is suitable for the determination of both ground and excited state properties of many-electron systems.

We shall adopt the following total energy functional with explicit self-interaction-correction (SIC) form¹⁸

$$(14)$$

where $E^{OEP}[\{\phi_{i\uparrow}, \phi_{j\downarrow}\}]$ is given in Eq. (12). Extending the OEP-KLI procedure, we arrive at

$$(15)$$

where

$$(16)$$

$$(17)$$

and

$$(18)$$

$$(19)$$

In essence, our proposed procedure is to solve self-consistently the set of OEP equations in Eqs. (10), with $V_{\sigma}^{OEP}(\mathbf{r})$ replaced by local potential $V_{SIC,\sigma}^{OEP}(\mathbf{r})$ in Eq. (15). Finally, we chose $\bar{V}_{SIC,\sigma}^{i=N_{\sigma}} = \bar{v}_{N_{\sigma}}$ for the highest occupied orbital as suggested by the KLI procedure. The energy of the

highest occupied orbital provides an approximate value for the first ionization potential.¹⁹

Nonrelativistic Atomic Structure Calculations ($Z = 2$ to 18)

We have applied the OEP/KLI-SIC method described above to the calculation of total energies and ionization potentials for neutral atoms and negative ions ($Z = 2$ to 18).¹³ For comparison, we also performed calculations of Kohn-Sham total energies and ionization potentials without the use of KLI-SIC, that is without the self-interaction correction. Both the LSDA and GGA energy functionals are used. For GGA, we used the BLYP energy functional, where B stands for the exchange energy functional of Becke⁹ and LY refers to the correlation energy functional of Lee-Yang-Parr.¹⁰

Table 1 shows some representative results of our KLI-SIC calculations for the ionization potentials of neutral atoms ($Z = 2$ to 18). It is seen that while the ionization potentials from the original LSDA and BLYP functionals have 30 to 50% discrepancy from the exact results, the corresponding results after the KLI-SIC procedure are markedly improved to within 1 to 5% of the exact values. To understand the physical origin of such an improvement, we show in Fig. 1 the effective potential $rV_{\text{eff}}(r)$ of LSDA and BLYP

with and without KLI-SIC for Ne and Ar atoms. Notice that both LSDA and BLYP potentials (without KLI-SIC) give rise to wrong long-range behavior ($rV_{\text{eff}}(r) \rightarrow 0$ asymptotically). On the other hand, the corresponding potentials with KLI-SIC reproduce the correct asymptotic behavior, namely, $rV_{\text{eff}}(r) \rightarrow -1$. This correct long-range behavior is crucial for proper DFT treatment of excited and continuum states as well as the autoionizing resonances to be described next.

Autoionizing Resonances

Because of the lack of proper long-range interaction behavior, previous photoionization calculations of complex atoms using LSDA or GGA energy functionals fail to exhibit the excited-state structure such as the prominent autoionizing resonances.^{20,21} Using the OEP/KLI-SIC procedure, we have recently performed a calculation of the photoionization spectrum of Ne using both time-independent LSDA and time-dependent LSDA (within linear response theory). Fig. 2 shows the comparison of the calculated results with experimental data. It is seen that the time-dependent LSDA (with KLI-SIC) results agree closely with the recent experimental data in the broad peak region, followed by a series of sharp resonances due to

Table 1. The Ionization Potentials (in a.u.) of Ground States of Neutral Atoms ($Z \leq 18$) Calculated from the Highest Occupied Orbital Energies by Various Exchange-correlation Energy Functionals

Atom	Non-KLI-SIC		KLI-SIC		Exp. ^a
	LSDA	BLYP	LSDA	BLYP	
He	0.517	0.585	0.918	0.950	0.904
Li	0.100	0.111	0.196	0.194	0.198
Be	0.170	0.201	0.308	0.323	0.343
B	0.120	0.143	0.290	0.304	0.305
C	0.196	0.218	0.412	0.422	0.414
N	0.276	0.297	0.536	0.543	0.534
O	0.210	0.266	0.479	0.523	0.501
F	0.326	0.377	0.645	0.680	0.640
Ne	0.443	0.492	0.808	0.837	0.793
Na	0.097	0.107	0.187	0.184	0.189
Mg	0.142	0.168	0.256	0.267	0.281
Al	0.086	0.102	0.192	0.198	0.217
Si	0.144	0.160	0.275	0.279	0.300
P	0.203	0.219	0.358	0.361	0.385
S	0.174	0.219	0.344	0.375	0.381
Cl	0.254	0.295	0.447	0.472	0.477
Ar	0.334	0.373	0.549	0.571	0.579

^a Ridzig, A. A.; Smirnov, B. M. *Reference Data on Atoms and Molecules*, Springer: Berlin, 1985.

Fig. 1. The one-electron effective potentials $r \cdot V_{\text{eff}}(r)$ of LSDA and BLYP with and without the KLI-SIC for (a) Ne atom, and (b) Ar atom.

$2s \rightarrow np$ resonance transitions (shown in Fig. 3). The calculated line widths and resonance line profile parameters are in good agreement with both experimental²² and CI (R-matrix)²³ results. To our knowledge this is the first successful DFT calculation which produces the fine structure of autoionizing resonances of complex atoms. This initial study indicates that DFT can now be refined to the level (OEP/KLI-SIC) that is capable of providing quantitative prediction of both static and dynamic properties of many-electron systems.

Relativistic DFT Calculations ($Z = 2-106$)

The relativistic density functional theory (RDFT) is the generalization of the non-relativistic Hohenberg-Kohn-Sham density-functional formalism^{6,7} to the relativistic regime.^{24,25} When the many-body effects are approximated locally as being those of a relativistic homogeneous electron gas, the relativistic local density approximation (RLDA) is obtained.^{24,25}

In the RDFT, one solves the following single-particle Dirac-Fock-like equation for N -electron atomic systems (in atomic units)

(20)

where $v_{eff,\sigma}$ is the effective one-particle local potential, σ is the spin index, and $\{\psi_{i\sigma}\}$ are the 4-component spinors. The total electron density is given by

(21)

and the total energy of the ground state is expressed as

(22)

Here T_s is the kinetic energy of the non-interacting N -electron systems including the rest-mass energy,

(23)

$J[\rho]$ is the classical electron-electron interaction energy, E_{xc} is the relativistic counterpart of the exchange-correlation energy, and v_{ext} is the external potential including the electron-nucleus interaction. The effective potential in Eq. (20) is given by

(24)

where $v_{xc,\sigma}$ is the relativistic exchange-correlation potential,

(25)

Similar to the non-relativistic case, the relativistic DFT describes above contains the undesirable self-interaction energy. Thus the relativistic exchange-correlation potential²⁴⁻²⁶ does not have the proper long-range behavior either. To overcome such problems, we have recently developed a self-interaction-free relativistic

Fig. 2. The total photoionization cross sections of time-independent and time-dependent calculations with LSDA/KLI-SIC potential.

Fig. 3. The photoionization cross sections near the $2s \rightarrow np$ resonant transitions, showing the autoionizing resonance profiles. The results are obtained by the TDLSDA with KLI-SIC potential. The experimental value of the $2s$ orbital energy is used in the calculation.

tic DFT based on the extension of the non-relativistic optimized effective potential (OEP) formalism with self-interaction correction (SIC) to the relativistic domain.²⁷

Using the relativistic OEP/KLI-SIC formalism, we performed a detailed atomic structure calculation of the orbital binding energies and ionization potentials (obtained from the highest occupied orbital energies) for the ground states of atoms with nuclear charge $Z = 2-106$.²⁷ The results are in good agreement with the experimental data to within a few percentage points across the periodic table ($Z = 2$ to 106). (See Fig. 4 for an example). To our knowledge, this is the first relativistic DFT calculation that has achieved such quantitative accuracy. With the development of the relativistic DFT/KLI-SIC formalism,²⁷ one can now in principle study the static properties and dynamical responses of any atoms in the periodic table with an accuracy comparable to the more sophisticated and much more time-consuming configuration-interaction (CI) calculations. The more challenging and important future new direction, however, is to extend the relativistic DFT with KLI-SIC to the time domain, allowing nonperturbative study of multiphoton dynamics of many-electron systems in superintense laser

fields ($I > 10^{18}$ W/cm²). This is an entirely unexplored area of strong-field atomic and molecular physics.

DFT Calculations of Molecular Structure Using OEP/KLI-SIC Procedure

The Kohn-Sham (KS) DFT formalism has been widely used for the calculation of the ground-state electronic structure of many-electron polyatomic molecules with great success in the past decade.¹⁻⁵ Due to the existence of the spurious self-interaction energy in the use of LSDA and GGA energy functionals, however, the long-range potential behavior is incorrect. As such, the excited-state and ionization potential properties of conventional molecular DFT calculations are not reliable. In the following we present some preliminary results of extending the OEP/KLI-SIC procedure to the molecular system. Due to the existence of multi-centers, the OEP/KLI-SIC calculations are more complicated than those in atomic cases.

In the diatomic molecular system, the effective potential within DFT has the following form,

(26)

where \mathbf{R}_1 and \mathbf{R}_2 are the locations of the two nuclei, $\mathbf{R}_1 = (a, 0, 0)$, $\mathbf{R}_2 = (-a, 0, 0)$ in Cartesian coordinates, with nuclear charges Z_1 and Z_2 , respectively. We use the prolate spheroidal coordinates (μ, ν, θ) , $0 < \mu < \infty$, $0 < \nu < \pi$, $0 < \theta < 2\pi$, for the description of the system. In order to symmetrize the Hamiltonian matrix, we transform the Kohn-Sham differential equation, Eq. (1), into a variational problem that minimizes the functional

(27)

The Coulomb repulsive potential $V_c = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$, satisfying the Poisson equation, $\nabla^2 V_c = -4\pi\rho$, can be also recast into the following variational form seeking the minimization of

(28)

Fig. 4. Ionization potentials calculated by (a) non-relativistic OEP/KLI-SIC and (b) relativistic OEP/KLI-SIC with exchange (x)-only (dashed line) and xc (solid line) energy functionals for neutral atoms with $2 \leq Z \leq 106$. The experimental ionization potentials are also presented (open circle) for comparison.

In the prolate spheroidal coordinates, we obtain the following integral form for F_s and F_c :

(29)

where we have assumed the total wavefunction can be expanded in the form, $\psi_{j\sigma}(\mathbf{r}) = e^{im\theta} \phi_{j\sigma}(\mu, \nu)$. We use the generalized pseudospectral technique^{28,29} to discretize the integral representation. This allows the use of non-uniform grid structure (denser mesh near each nucleus) and results in a symmetric eigenvalue problem, subject to some appropriate boundary conditions. The KLI-SIC method is extended for the OEP treatment of the effective potential $v_{eff,\sigma}$. Detailed procedure will be presented elsewhere.³⁰

Table 2 shows some representative results of the ionization potentials for both homonuclear and heteronuclear diatomic molecules using LSDA and BLYP energy functionals with or without OEP/KLI-SIC. Similar to the atomic case, the ionization potentials obtained from the conventional Kohn-Sham DFT calculations using LSDA or BLYP energy functionals are in large discrepancy (40-50% too low) from the experimental results. With the implementation of OEP/KLI-SIC, the results are significantly improved to within a few percentages points of the experimental data. Further improvement of the OEP/KLI-SIC procedure for studying the electronic structure, potential energy surface, and dynamical properties of polyatomic molecules is currently under investigation.

Electronic Structure of Quantum Dots

Recent advances in semiconductor technology have

Table 2. Comparison of Ionization Potentials (in a.u.) (Obtained from the Highest Occupied Orbital Energies) Calculated from Various DFT Procedures. The Last Column Shows the Experimental Values

	LSDA	BLYP	LSDA/KLI-SIC	BLYP/KLI-SIC	Expt.
H ₂	0.3731	0.3800	0.6205	0.6225	0.5669
Li ₂	0.1187	0.1130	0.1968	0.1900	0.18
Be ₂	0.1660	0.1612	0.2781	0.2634	—
C ₂	0.2987	0.2771	0.4716	0.4582	0.4465
N ₂	0.3826	0.3751	0.6454	0.6262	0.5726
LiH	0.1612	0.1585	0.3236	0.3193	0.283
BH	0.2041	0.1995	0.3488	0.3804	0.359
HF	0.3594	0.3524	0.6469	0.6392	0.5894

led to the fabrication of a zero-dimensional structure called quantum dots.^{31,32} Essentially they are little islands of quasi-two-dimensional electrons which are laterally confined by an artificial potential. The electronic structure of these confined electrons is very important and interesting in the area of basic and applied physics. The confining potential of the order of a few meV can be chosen experimentally. Many-body effects due to the electron-electron interactions show a broad range of electronic structures similar to those of real atoms. The number of electrons in a quantum dot, N , which can be controlled experimentally, affects many physical properties of the quantum dot. The dependence of the chemical potential on N can be measured directly through single-electron spectroscopy.^{33,34} By changing the quantum dot size and the number of electrons, far IR absorption,³⁵ capacitance spectroscopy,³⁶ and conductance measurements³⁷ determine the tunneling conductance and capacitance resulting from the competition of quantum confinements and Coulomb interactions.

A recent measurement by Tarucha et al.³⁴ have probed the electronic structure of quantum dots through single-electron tunneling spectroscopy. An instructive finding is the existence of a shell structure of addition energies. The addition energy, $\mu(N)$, is defined to be the energy needed to add an electron into the $(N-1)$ electron system, namely, $\mu(N) = E_{tot}(N) - E_{tot}(N-1)$, where $E_{tot}(N)$ is the total energy of the N -electron quantum dot. [In atomic physics language, the addition energy $\mu(N)$ corresponds to the ionization potential of N -electron atoms.] Several recent theoretical studies have explored the shell-filling behavior of a few-electron (less than 20) quantum dots.³⁷⁻³⁹ No detailed exploration has been performed yet on the general shell-filling behavior for many-electron quantum dots. Further, all the DFT studies of quantum dots so far^{38,39} have employed the conventional LSDA or GGA energy functional which possesses incorrect long-range potential behavior. In the following we extend the OEP/KLI-SIC formalism to the study of the electronic structure and shell-filling behavior of quantum dots with $N = 2$ to 60.

The Hamiltonian for a quantum dot, in the effective atomic units, can be written as follows:

$$(30)$$

where

$$(31)$$

Here we adopt an anisotropic parabolic potential with the cylindrical symmetry of the characteristic frequencies ω_x and ω_z . For the special case of $\omega_x = \omega_z = \omega$, the confining potential is the spherical 3D harmonic potential. The unit of length is the effective Bohr radius $a_B^* = \hbar^{-2} \epsilon_s / m^* e^2$ and the unit of energy is twice the effective Rydberg $2Ry^* = e^2/a_B^*$. For GaAs quantum dots, for example, the effective atomic units are calculated as $a_B^* = 99.0 \text{ \AA}$ and $2Ry^* = 11.61 \text{ meV}$, from values of the static dielectric constant $\epsilon_s = 12.53$ and of the electron effective mass $m^* = 0.067m_e$. We have studied quantum dots for both isotropic and anisotropic confining potentials. In DFT calculations, the Hamiltonian H in Eq. (30) is replaced by H_{KS} in Eq. (1), and the “external” potential $v_{ext}(\mathbf{r})$ in Eq. (4) is given by the confining harmonic potential in Eq. (31). Some of the new results of the isotropic case are presented below.

Table 3 shows the comparison of four different DFT calculations of the total energy, orbital energy, and addition energy, corresponding to the two-electron quantum-dot system with the 3D spherical harmonic oscillator as the confining potential ($\omega = 0.75$). The four DFT calculations correspond to the use of LSDA and BLYP energy functionals with or without OEP/KLI-SIC. Also shown for comparison are the exact results for the total and addition energies. Without the OEP/KLI-SIC, the LSDA total energy is smaller than the exact energy, while the BLYP total energy is larger than the exact value. Further, the highest occupied orbital energy obtained from both LSDA and BLYP energy functionals differ substantially from the addition energy. With the implement of the OEP/KLI-SIC procedure, the total energies from both LSDA and BLYP energy functional forms are significantly improved, with the BLYP/KLI-SIC result closest to the exact value. More importantly, the highest occupied orbital energies from both LSDA/KLI-SIC and BLYP/KLI-SIC calculations are close to the exact addition energy. Physically this means that the highest occupied orbital energy of N -electron quantum dots can be used as a direct measure of the addition energy. This is because the long-range potential in the OEP/KLI-SIC procedure has the proper Coulombic behavior and the electronic structure of quantum dots is more accurately described, including the binding energies of the valence electrons.

Fig. 5 shows the capacitive energy, $\mu(N) - \mu(N-1)$, as a function of the electron number N calculated by the BLYP/KLI-SIC procedure, exhibiting the detailed shell and subshell electronic structure of many-electron 3D quantum dots for the first time. Similar shell-filling structure is obtained when the other three DFT procedures are used.

Table 3. Comparison of the Calculated Total Energies, Orbital Energies and Addition Energies of a Two-electron Quantum Dot System in Spherical Harmonic Potential Corresponding to $\omega = 0.75$. The Energies are in Effective Atomic Units

	E_{total}	$E_{orbital}$	E_{add}
LSDA	2.831	1.966	1.701
BLYP	2.894	1.992	1.769
LSDA/KLI-SIC	2.865	1.750	1.740
BLYP/KLI-SIC	2.878	1.751	1.753
EXACT	2.875	—	1.750

To understand the origin of the shell-filling structure, we need to first explore the energy order of individual electron orbitals. In the absence of e-e interaction, the energy order can be identified as 1s, 2p, (3d,2s), (4f,3p), (5g,4d,3s), (6h,5f,4p), etc., where those energy levels in the parenthesis are degenerate. This ordering can be obtained by considering the energy levels of the 3D spherical harmonic oscillator. In the presence of a many-body electron-electron interaction, the degeneracy of (3d,2s), (4f,3p), (5g,4d,3s) etc., will be lifted. From our calculations, we found that the electron orbital with larger angular momentum is lower in energy. This is reminiscent of Hund's rule. Fig. 6 shows the pattern of orbital energy ordering; the upper diagram corresponds to the 3D spherical harmonic oscillator (without e-e interaction), while the lower diagram shows the pattern for quantum dots confined by a spherical harmonic potential.

Fig. 5. Capacitive energies $(\mu(N) - \mu(N-1))$ of N -electron quantum dots confined by a spherical harmonic potential ($\omega = 0.75$), exhibiting the shell-filling structure. The BLYP/KLI-SIC procedure is used in the DFT calculation. Solid line corresponds to the results where $\mu(N) = E_{tot}(N) - E_{tot}(N-1)$. The dashed line shows the results where $\mu(N)$ is taken directly from the highest occupied orbital energy. It is seen the two different results nearly coincide with each other.

Using this energy ordering, we are able to identify all the shell structures in Fig. 5. Those peak positions marked \oplus correspond to the quantum dots with filled shells or subshells. The most prominent shell structure occurs at the following “magic” numbers $N = 2$ ($1s^2$), 8 ($1s^2 2p^6$), 20 ($1s^2 2p^6 3d^{10} 2s^2$), 40 ($1s^2 2p^6 3d^{10} 2s^2 4f^{14} 3p^6$), etc., corresponding to the fully occupied shells. The smaller peaks marked \oplus in Fig. 5 can also be identified as those quantum dots with half-filled subshells. It is instructive to find that Hund’s rule is also applicable to the quantum dot systems. More detailed study of the electronic structure of quantum dots including the anisotropic confining potential case will be discussed elsewhere.

RECENT NEW DEVELOPMENTS IN TIME-DEPENDENT DENSITY FUNCTIONAL THEORY FOR MULTIPHOTON PROCESSES IN INTENSE LASER FIELDS

The time-dependent density-functional theory (TDDFT) as a rigorous formalism is a more recent development in density-functional theory, although the historical roots date back to the time-dependent Thomas-Fermi model

proposed by Bloch in 1933.⁴⁰ The central result of modern TDDFT is a set of time-dependent Kohn-Sham (TDKS) equations which are structurally similar to the time-dependent Hartree-Fock (TDHF) equations but include (in principle exactly) all many-body effects through a local time-dependent exchange-correlation (xc) potential. To date, most applications of TDDFT fall in the regime of weak-field linear or nonlinear response and the local spin-density approximation (LSDA) is often used.^{20,21,41,42} Applications of the time-dependent LSDA approach have been made to the photo-response of atoms and molecules, metallic, semiconductor surfaces, and bulk semiconductor in the weak-field perturbative regime.^{20,21,41,42}

The conventional (weak-field) TDKS formalism, however, cannot be applied to the study of multiphoton processes in strong laser fields, a subject of much current interest and significance in chemical physics and atomic, molecular, and optical physics. Two major fundamental difficulties in the TDKS formalism need to be addressed and overcome: (a) Similar to the steady-state DFT, the TDKS formalism using LSDA or GGA energy functionals contains spurious self-interaction energy, leading to incorrect long-range interactions and multiphoton dynamics. (b) Nonperturbative TDDFT beyond the weak-field perturbative TDKS formalism^{20,21,41,42} needs to be developed for the treatment of strong-field processes. To this end, we have recently developed a TDDFT with optimized effective potential (OEP) and self-interaction correction (SIC) for nonperturbative treatment of many-electron systems in intense laser fields,⁴³ based on the extension of the steady-state OEP/KLI-SIC procedure¹³ to the time domain.

TDDFT with OEP/KLI-SIC for Multiphoton Processes in Intense Ultrashort Pulsed Laser Fields

The quantum mechanical action of a many-electron system interacting with an external field can be expressed as^{43,44}

Fig. 6. Schematic energy level diagram for (a) spherical harmonic potential (without e-e interaction); (b) quantum dots confined by spherical harmonic oscillator (with e-e interaction).

where $\{\psi_{i\sigma}(\mathbf{r}, t)\}$ are the time-dependent spin-orbitals, $N = \sum_{\sigma} N_{\sigma}$ is the total number of electrons, $v_{ext}(\mathbf{r}, t)$ is the “external potential” [which includes the electron-nucleus Coulomb interaction and the coupling of the electron to the external laser fields], $\rho(\mathbf{r}, t) = \sum_{\sigma} \rho_{\sigma}(\mathbf{r}, t)$ is the total electron density with the spin-density

(33)

and $A_{xc}[\{\psi_{i\sigma}\}]$ is the exchange-correlation (xc) energy action functional. The spin orbitals satisfy the one-electron Schrödinger-like equation:

(34)

where $V_{\sigma}(\mathbf{r}, t)$ will be the time-dependent optimized effective potential (OEP) if we choose the set of spin-orbitals $\{\psi_{i\sigma}\}$ which render the total action functional $A[\{\psi_{i\sigma}\}]$ stationary:

(35)

An essential step is that we propose the following SIC expression for the exchange-correlation (xc) action functional,⁴³

(36)

where E_{xc} is the time-dependent exchange-correlation energy functional and

(37)

The use of the SIC form in Eq. (36) removes the spurious self-interaction terms in conventional DFT and results in proper long-range potential. Another major advantage of this procedure is that only local potential is required to construct the orbital-independent OEP. This facilitates the numerical computation considerably.

By extending the KLI procedure to the time-dependent case, we obtain the time-dependent OEP as:

where

(38)

(39)

and

(41)

(42)

In Eqs. (41) and (42), $\bar{V}_{SIC, \sigma}^i$ and $\bar{v}_{i\sigma}$ are constants at a given time t , although the value of $\bar{V}_{SIC, \sigma}^i$ is unknown. The KLI method suggests a way to calculate $\bar{V}_{SIC, \sigma}^i(t) - \bar{v}_{i\sigma}^i(t)$ through a solution of the following linear equations

(43)

where

(44)

(45)

In the time-dependent OEP/KLI-SIC method outline here, Eqs. (33), (34) and (38) are to be solved self-consistently. Note that Eq. (34) is an initial value problem and the initial wave function can be determined by

(46)

where, $\phi_{i\sigma}(\mathbf{r})$ and $\epsilon_{i\sigma}$ are the eigenfunction and eigenvalue of the time-independent Kohn-Sham equation (with OEP/KLI-SIC) for the static case.¹³

We have begun to apply the TDDFT/KLI-SIC formalism to the study of atomic and molecular multiphoton pro-

cesses in intense laser fields, particularly the phenomenon of multiple high-order harmonic generation (HHG) in intense laser fields. The HHG phenomena is one of the most rapidly developing topics in strong-field atomic and molecular physics.⁴⁵⁻⁵¹ The generation of harmonic orders well in excess of 100 from noble gas, polyatomic molecules, and cluster targets has been demonstrated by several recent experiments.⁴⁷⁻⁵¹ For example, in a recent experiment,⁵⁰ ultrashort laser pulses (with 26 fs pulse duration) from a Ti:sapphire laser have been used to generate coherent radiation at wavelengths as short as 2.7 nm (460 eV). These wavelengths are well within the "water window" region of x-ray transmission. Thus the HHG mechanism provides a simple and powerful new route to generate a coherent x-ray laser source which is technically much less demanding and less energy intensive than current plasma based x-ray schemes. The availability of such a compact laboratory (table-top) system for the generation of coherent x-rays holds promise as a source for biological holography and nonlinear optics in the x-ray regime. Another potential new application of HHG processes is the possibility of generating laser pulses of ultrashort duration (tens of attoseconds) in the near future, leading the way to perform attosecond spectroscopy and study new dynamical phenomena with attosecond time resolution.

To study the strong-field process of N -electron quantum systems using *ab initio* wavefunction approach, it is necessary to solve the time-dependent Schrödinger equation with $3N$ spatial dimensions in space and time. This is far beyond the capability of current supercomputer technology. In fact, even for the two-electron systems (involving the solution of 6D time-dependent partial differential equation), *ab initio* study is only at the beginning stage and far from satisfaction.⁵² One approximation that has been used widely for multi-electron system is the single-active-electron (SAE) model with frozen core, basically involving the solution of one-electron Schrödinger equation with model potential. Within the SAE model, however, important physical effects such as electron correlation, core excitation, resonance states etc., are completely ignored. It is desirable to develop more complete formalism for detailed treatment of strong-field processes, taking into account both electron correlation and the structure of excited states and at the same time allowing for core excitation. Our proposed TDDFT with OEP/KLI-SIC formalism^{43,53} provides an essential step towards this goal. Much remains to be explored in this direction.

Our initial application of the TDDFT/KLI-SIC formalism is to study the role of dynamical electron correlation

on HHG of He atoms in intense linearly polarized (LP) laser pulses.⁴³ In particular, we have studied the mechanism responsible for the production of the "higher" harmonics observed in the experiment⁵⁴ which can not be explained by the SAE model.^{45,55} Fig. 7(b) shows that while the SAE model fails to produce the higher harmonics, the TDDFT/KLI-SIC results agree well with the experimental data in both lower and higher HHG regimes, indicating the important role played by the dynamical electron correlation.⁴³

In all the theoretical and experimental studies so far,⁴³⁻⁵⁵ only LP HHG has been studied. This is because the dipole selection rule excludes the possibility of producing circularly polarized (CP) harmonics by multiphoton mechanism. Recently, however, we have proposed the first feasible experimental scheme which can generate purely CP high harmonics, using two-color laser fields (Fig. 8). The proposed experimental set-up consists of a CP fundamental laserfield (ω) and a LP second-harmonic laser field (2ω), in

Fig. 7. (a) Comparison of the bound-state populations $N_{1s}(t)$ of He atoms obtained from the all-electron calculations (thick line) with those from the SAE model (thin line). The envelope of the laser pulse is also presented (dashed line). (b) The HHG spectrum of He obtained from the all-electron calculation (open circle) and from the SAE model (filled triangle). The experimental data (with error bar) are also shown for comparison. The HHG yields are normalized to the 13th harmonic peak. In both (a) and (b), the laser peak intensity used in the calculation is $I = 3.5 \times 10^{15} \text{ W/cm}^2$ and wavelength $\lambda = 248.6 \text{ nm}$.

crossed-beam configuration.⁵⁶ The feasibility of such a scheme is confirmed by our 3D TDDFT/KLI-SIC calculation.⁵⁶ (See Fig. 9 for an example). Much remains to be explored in the study of HHG mechanisms and the coherent control of HHG processes to achieve desirable goals.

Floquet Formulation of TDDFT

In the previous Section, the time-dependent equations in TDDFT/KLI-SIC formulation are solved numerically by propagating individual orbital wavefunction in time in a self-consistent fashion. We call this procedure the time-dependent approach to TDDFT. It is a natural approach for problems involving short pulsed laser fields where the atom (molecule)-field interaction Hamiltonian can be an arbitrary function of time. There are other important class of problems, however, that the Hamiltonian is a periodic function of time, such as the case involving long pulsed laser fields. In this case, it is advantageous to employ the generalized Floquet theory,^{57,58} which allows the exact transformation of the periodically (or quasi-periodically) time-dependent Schrödinger equation into an equivalent time-independent Floquet matrix eigenvalue problems. The time-independent Floquet formulation and its various generalized formalisms^{57,58} developed in the last two decades have been used extensively for the nonperturbative treatment of numerous atomic and molecular multiphoton and nonlinear optical processes in intense one-color and multi-color laser fields.^{57,58} The time-independent Floquet approaches, when they are applicable, have several advantages over the time-dependent approaches. First, the Floquet approach is numerically more accurate since only it involves only the solution of a (Hermitian or non-Hermitian) time-independent Floquet matrix

eigenvalue problem. Second, the Floquet-state or dressed-state picture provides useful physical insights regarding the multiphoton dynamics in terms of the avoided crossing pattern of quasi-energy levels. Third, for near-resonant multiphoton processes, nearly-degenerate (high-order) perturbation theory can be applied to the Floquet Hamiltonian, leading to analytical expressions and insights valuable for both theoretical and experimental investigation of multiphoton and nonlinear optical phenomena.

The idea of the combination of the Floquet formulation with TDDFT thus opens up a powerful new nonperturbative time-independent approach to the study of multiphoton and nonlinear optical processes of many-electron quantum systems (atoms, molecules, solids, condensed matter etc.) in the future.⁵⁹ The first Floquet formulation of TDDFT has been recently developed.⁵⁹ It is

Fig. 8. The proposed crossed laser beam scheme for the production of circularly polarized multiple high-order harmonic generation.

Fig. 9. Circularly polarized HHG power spectra of He atoms produced in the crossed laser beam configuration. The incident CP laser intensities used are: (a) $I_1 = 2 \times 10^{12}$ W/cm²; (b) $I_1 = 2 \times 10^{13}$ W/cm² and (c) $I_1 = 2 \times 10^{14}$ W/cm². The incident LP field intensity is fixed at $I_2 = 2 \times 10^{14}$ W/cm². The laser wavelengths used are 1064 nm for the incident CP field and 532 nm for the incident LP field. For comparison, the one-color LPHHG data (denoted by filled circles) are also included. Fig. 9(b) shows the optimal generation of the CP high harmonics by two-color crossed laser fields.

shown that the time-dependent Kohn-Sham equation can be exactly transformed into an equivalent time-independent Floquet matrix eigen problem whose eigenvalues (quasi-energies) are unique functionals of the electron spin-density. Further for the bound-continuum transitions, the notions of "complex" density and "complex" equation of continuity can be introduced to facilitate the study of multiphoton ionization (dissociation) processes.⁵⁹ Initial application to the study of multiphoton ionization of He atoms⁵⁹ yields results in good agreement of the experimental data. Most recent extensions of the Floquet-TDDFT formalism include the many-mode Floquet treatment of the multi-color laser excitation case⁶⁰ as well as the consideration of the time-dependent current density functional.⁶¹ The latter development is necessary when the current density and magnetic field play an important role.

Application of the Floquet-TDDFT formalisms to the study of molecular multiphoton processes such as above-threshold (electron) ionization and (chemical bond) dissociation, HHG, and nonlinear optical susceptibilities etc., is in progress and will be reported elsewhere.

ACKNOWLEDGMENTS

The works reported here were partially supported by US Department of Energy, National Science Foundation, and Kansas Center for Advanced Scientific Computing. We are grateful to the fruitful discussions with Hardy Gross, Weitao Yang, Joseph Krieger, and John Perdew on various aspects of DFT.

Received December 31, 1998.

Key Words

Density functional theory; Floquet theory;
Multiphoton processes; High harmonic generation;
Strong-field atomic and molecular physics.

REFERENCES

1. Parr, R. G.; Yang, W. T. *Density-Function Theory of Atoms and Molecules*; Oxford University Press, New York, **1989**.
2. Dreizler, R.; Gross, E. K. U. *Density Functional Theory - An Approach to the Quantum Many-Body Problem* Springer: Berlin, **1990**.
3. *Density Functional Theory*, Vol. 337 of NATO ASI Series B, Gross, E.; Dreizler, R. M. Eds.: Plenum Press: New York, **1995**.
4. March, N. H. *Electron Density Theory of Atoms and Molecules*, Academic Press: San Diego, **1992**.
5. *Density Functional Methods in Chemistry*, Labanowski, J. K.; Andzelm, J. W. Eds. Springer: Berlin, **1991**.
6. Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
7. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
8. Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
9. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
10. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
11. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1986**, *33*, 8800.
12. Zhao, Q.; Parr, R. G. *Phys. Rev. A* **1992**, *46*, R5320.
13. Tong, X. M.; Chu, S. I. *Phys. Rev. A* **1997**, *55*, 3406.
14. Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.
15. Sharp, R. T.; Horton, G. K. *Phys. Rev.* **1953**, *90*, 317.
16. Talman, J. D.; Shadwick, W. F. *Phys. Rev. A* **1976**, *14*, 36.
17. Krieger, J.; Li, Y.; Iafrate, G. *Phys. Lett. A* **1990**, *146*, 256; *Phys. Rev. A* **1992**, *45*, 101; *Phys. Rev. A* **1992**, *46*, 5453.
18. Norman, M.; Koelling, D. *Phys. Rev. B* **1984**, *30*, 5530.
19. Perdew, J.; Parr, R.; Levy, M.; Balduz, J. J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691.
20. Zangwill, A.; Stoven, P. *Phys. Rev. A* **1980**, *21*, 1561.
21. Mahan, G. D.; Subbaswamy, K. R. *Local Density Theory of Polarizability*, Plenum Press: New York, **1990**.
22. Codling, K.; Madden, R. P.; Ederer, D. L. *Phys. Rev.* **1967**, *155*, 26.
23. Burke, P. G.; Taylor, K. T. *J. Phys. B* **1975**, *8*, 2620.
24. Rajagopal, A. K.; Callaway, J. *Phys. Rev. B* **1973**, *7*, 1912.
25. MacDonald, A. H.; Vosko, S. H. *J. Phys. C* **1979**, *12*, 2977.
26. Ramana, M. V.; Rajagopal, A. K. *Adv. Chem. Phys.* **1983**, *54*, 231.
27. Tong, X. M.; Chu, S. I. *Phys. Rev. A* **1998**, *57*, 855.
28. Yao, G.; Chu, S. I. *Chem. Phys. Lett.* **1993**, *204*, 381.
29. Wang, J.; Chu, S. I.; Laughlin, C. *Phys. Rev. A* **1994**, *50*, 3208.
30. Chu, X.; Chu, S. I. (to be published).
31. Kastner, M. *Phys. Today* **1993**, *46*, 24.
32. Jacak, L.; Hawrylak, P.; Wojs, A. *Quantum Dots*, Springer: New York, **1989**.
33. Ashoori, R. C. et al. *Phys. Rev. Lett.* **1993**, *71*, 613.
34. Tarucha, S. et al. *Phys. Rev. Lett.* **1996**, *77*, 3613.

35. Lorke, A.; Kotthaus, J. P.; Ploog, K. *Phys. Rev. Lett.* **1990**, *64*, 2559.
36. Hansen, W. et al. *Phys. Rev. Lett.* **1989**, *62*, 2168.
37. Fujito, N.; Natori, A.; Yasunaga, H. *Phys. Rev. B* **1996**, *53*, 9952.
38. Macucci, M.; Hess, K.; Iafrate, G. J. *Phys. Rev. B* **1997**, *55*, 4879.
39. Lee, I. H. et al. *Phys. Rev. B* **1998**, *57*, 9035.
40. Bloch, F. *Z. Physik* **1933**, *81*, 363.
41. Deb, B. M.; Ghosh, S. K. *J. Chem. Phys.* **1982**, *77*, 342.
42. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997.
43. Tong, X. M.; Chu, S. I. *Phys. Rev. A* **1998**, *57*, 452.
44. Ullrich, C. A.; Grossmann, U. J.; Gross, E. K. U. *Phys. Rev. Lett.* **1995**, *74*, 872.
45. L'Huillier, A.; Schafer, K. J.; Kulander, K. C. *J. Phys. B.* **1991**, *24*, 3315.
46. Perry, M. D.; Mourou, G. *Science* **1991**, *264*, 917.
47. Zhou, J. et al. *Phys. Rev. Lett.* **1996**, *76*, 752.
48. Christov, I. P. et al. *Phys. Rev. Lett.* **1996**, *77*, 1743.
49. Kan, C. et al. *Phys. Rev. Lett.* **1997**, *79*, 2971.
50. Chang, Z. et al. *Phys. Rev. Lett.* **1997**, *79*, 2967.
51. Schnürer M. et al. *Phys. Rev. Lett.* **1998**, *80*, 3236.
52. Parker, J. et al. *J. Phys. B* **1996**, *29*, L33.
53. Tong, X. M.; Chu, S. I. *Int. J. Quantum Chem.* **1998**, *69*, 293.
54. Sarukura, N. et al. *Phys. Rev. A* **1991**, *43*, 1669.
55. Krause, J. L.; Schafer, K. J.; Kulander, K. C. *Phys. Rev. A* **1992**, *45*, 4998.
56. Tong, X. M.; Chu, S. I. *Phys. Rev. A* **1998**, *58*, R2656.
57. For reviews on various generalized Floquet formalisms, see (a) Chu, S. I. *Adv. At. Mol. Phys.* **1985**, *21*, 197. (b) Chu, S. I. *Adv. Chem. Phys.* **1989**, *73*, 739.
58. Chu, S. I. in *Multiparticle Quantum Scattering with Applications to Nuclear, Atomic, and Molecular Physics*, Truhlar, D. G.; Simon, B. Eds.: Springer, New York, **1997**, pp. 343-387.
59. Telnov, D. Chu, S. I. *Chem. Phys. Lett.* **1997**, *264*, 466.
60. Telnov, D. A.; Chu, S. I. *Int. J. Quantum Chem.* **1998**, *69*, 305.
61. Telnov, D. A.; Chu, S. I. *Phys. Rev. A* **1998**, *58*, 4749.

Fig. 1.

The one-electron effective potentials $r \cdot V_{\text{eff}}(r)$ of LSDA and BLYP with and without the KLI-SIC for (a) Ne atom, and (b) Ar atom.

Fig. 2.

The total photoionization cross sections of time-independent and time-dependent calculations with LSDA/KLI-SIC potential.

Fig. 3.

The photoionization cross sections near the $2s \rightarrow np$ resonant transitions, showing the autoionizing resonance profiles. The results are obtained by the TDLSDA with KLI-SIC potential. The experimental value of the $2s$ orbital energy is used in the calculation.

Fig. 4.

Ionization potentials calculated by (a) non-relativistic OEP/KLI-SIC and (b) relativistic OEP/KLI-SIC with exchange (x)-only (dashed line) and xc (solid line) energy functionals for neutral atoms with $2 \leq Z \leq 106$. The experimental ionization potentials are also presented (open circle) for comparison.

Fig. 5. Capacitive energies $(\mu(N) - \mu(N-1))$ of N -electron quantum dots confined by a spherical harmonic potential ($\omega = 0.75$), exhibiting the shell-filling structure. The BLYP/KLI-SIC procedure is used in the DFT calculation. Solid line corresponds to the results where $\mu(N) = E_{\text{tot}}(N) - E_{\text{tot}}(N-1)$. The dashed line shows the results where $\mu(N)$ is taken directly from the highest occupied orbital energy. It is seen the two different results nearly coincide with each other.

Fig. 6.

Schematic energy level diagram for (a) spherical har-

monic potential (without e-e interaction); (b) quantum dots confined by spherical harmonic oscillator (with e-e interaction).

Fig. 7.

(a) Comparison of the bound-state populations $N_{1s}(t)$ of He atoms obtained from the all-electron calculations (thick line) with those from the SAE model (thin line). The envelope of the laser pulse is also presented (dashed line). (b) The HHG spectrum of He obtained from the all-electron calculation (open circle) and from the SAE model (filled triangle). The experimental data (with error bar) are also shown for comparison. The HHG yields are normalized to the 13th harmonic peak. In both (a) and (b), the laser peak intensity used in the calculation is $I = 3.5 \times 10^{15} \text{ W/cm}^2$ and wavelength $\lambda = 248.6 \text{ nm}$.

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The proposed crossed laser beam scheme for the production of circularly polarized multiple high-order harmonic generation.

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Circularly polarized HHG power spectra of He atoms produced in the crossed laser beam configuration. The incident CP laser intensities used are: (a) $I_1 = 2 \times 10^{12} \text{ W/cm}^2$; (b) $I_1 = 2 \times 10^{13} \text{ W/cm}^2$ and (c) $I_1 = 2 \times 10^{14} \text{ W/cm}^2$. The incident LP field intensity is fixed at $I_2 = 2 \times 10^{14} \text{ W/cm}^2$. The laser wavelengths used are 1064 nm for the incident CP field and 532 nm for the incident LP field. For comparison, the one-color LP HHG data (denoted by filled circles) are also included. Fig. 9(b) shows the optimal generation of the CP high harmonics by two-color crossed laser fields.

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